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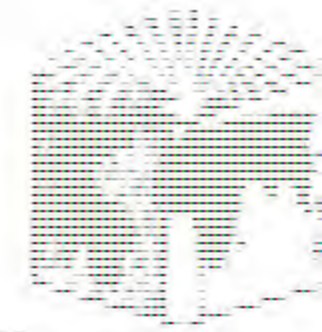
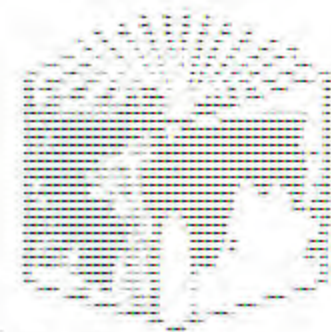
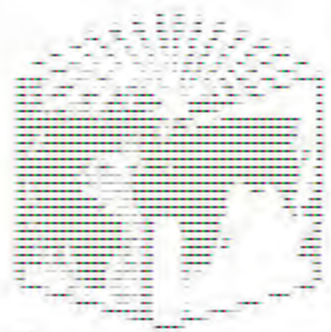
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Empirical law of Dulong & Petit

Many elements do have atomic heats in the vicinity of $6.0 \text{ cal/gm}^\circ\text{C}$ but certain elements, particularly some of those with low atomic weights, have atomic heats that are appreciably less than this value.

30/06/93

To V.

Read and written by: K. Jain

Organic
sy. or B.Sc - Bell.
K. Jain
13/11/93

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PREFACE

Although a number of excellent books on quantum mechanics, statistical mechanics and molecular spectra are available, much of the material contained in them is not of immediate interest to the majority of chemists. The purpose of this book is to provide an introduction to certain aspects of these subjects that have a bearing on chemical problems. Such topics as the quantum theory of valence, the concept of resonance, the electronic configurations of molecules, the calculation of thermodynamic functions from spectroscopic data, dissociation accompanying light absorption, valence force constants, bond distances, and intermolecular forces, to mention a few, are of direct importance to chemistry.

It cannot be claimed that the treatment given here is comprehensive or completely rigorous. This book alone is not necessarily sufficient to supply the detailed instruction which would permit the reader to use quantum mechanics and statistical mechanics as tools for himself. Its primary object is to help him understand clearly how they have been employed by others to obtain results of chemical significance. At the same time, the knowledge gained from the present work will provide the foundation upon which may be based a more detailed treatment of the subjects to be found in the publications mentioned in the text and at the end of the preface.

It is inevitable that a book dealing with topics which are largely theoretical should be somewhat mathematical in character. However, the mathematics used should be within the scope of the reader with an elementary knowledge of calculus, including simple differential equations. Since these are prerequisites for majoring in chemistry in most colleges whose courses are approved by the American Chemical Society, the material should be understood by any graduate in chemistry. In any event, pure formalism in the mathematics has been avoided so far as possible; whenever feasible an attempt has been made to give a physical basis to the problem under consideration and to illustrate the results by means of practical examples. While it is admitted that the subject matter of this book is not easy reading, the contents should be readily comprehended by those who are prepared to devote a little time to its study.

In preparing this book invaluable assistance has been derived from a number of standard works to which the reader is referred for further information. Special mention may be made of Dushman, "Elements of Quantum Mechanics"; Fowler and Guggenheim, "Statistical Thermodynamics"; Herzberg, "Atomic Spectra and Atomic Structure," and "Molecular Spectra and Molecular Structure: Diatomic Molecules"; Kronig, "Optical Basis of the Theory of Valency"; Mayer and Mayer, "Statistical Mechanics"; Pauling and Wilson, "Introduction to Quantum Mechanics";

Penney, "Quantum Theory of Valency"; Sutherland, "Infra-Red and Raman Spectra"; Tolman, "The Principles of Statistical Mechanics"; and Wu, "Vibrational Spectra and Structures of Polyatomic Molecules." To the authors of these books the writer expresses his great indebtedness. In addition, use has been made of some portions of Glasstone, Laidler and Eyring, "The Theory of Rate Processes." Two other books, published since the manuscript of the present work was completed, are recommended to the reader; these are Margenau and Murphy, "The Mathematics of Physics and Chemistry," and Eyring, Walter and Kimball, "Quantum Chemistry." Finally, the writer wishes to record his appreciation of the help given him by his wife in the preparation of the manuscript and in the correction of proof.

SAMUEL GLASSTONE

BERKELEY, CALIF.
April 1944

CHAPTER I

INTRODUCTION: QUANTUM NUMBERS

ATOMIC QUANTUM NUMBERS¹

1a. Principal and Azimuthal Quantum Numbers.—The energy of an electron moving in the central force field of a single atom is determined essentially by two quantum numbers, designated by the letters n and l , respectively. As will be seen in Chapter II, the *principal quantum number* n must of necessity be integral, while for a given value of n , the so-called *azimuthal quantum number* l may have any one of the values $n - 1, n - 2, \dots, 1, 0$. In classical mechanics the principal quantum number represents the ordinal number of the particular orbit occupied by the electron, but in wave mechanics the concept of definite orbits is discarded. The number n can, nevertheless, be regarded as giving an indication of the mean distance of the electron from the atomic nucleus. Thus, an electron having a principal quantum number equal to unity will, on the average, be closer to the nucleus than will an electron whose principal quantum number is two. Similarly, the latter will, in general, be nearer to the nucleus than will an electron of quantum number three, and so on. It will be apparent from the equations to be derived in the following chapter, that the binding energy of an electron in a hydrogen-like atom decreases as n is increased; this is in harmony with the view that increasing values of the principal quantum number represent larger mean distances of the electron from the nucleus.

Instead of describing an electron by the numerical value of its principal quantum number, e.g., 1, 2, 3, \dots , etc., it is sometimes the practice to employ the letters K, L, M, \dots , etc. Thus, a K electron is an electron having a principal quantum number of unity; for an L electron the value of n is two, and so on. These letters are also employed to describe a group of electrons in an atom having the same principal quantum number; it is thus possible, for example, to refer to the K shell or the L shell of an atom.

The azimuthal quantum number l gives a measure of the angular momentum of an electron in its orbital motion about the nucleus, generally referred to as the *orbital angular momentum*. In spite of the fact that orbits have no precise wave-mechanical significance, the orbital angular momentum may be described by a definite vector quantity having the value $\sqrt{l(l+1)}\hbar/2\pi$. For the purpose of identifying the various electrons in an atom, the general procedure is to employ a symbol consisting of an integer, which is the principal quantum number n , followed by a letter representing the value of l ; the letters used are s, p, d, f , etc., corresponding to l equal to

¹ Herzberg, "Atomic Spectra and Atomic Structure"; "Molecular Spectra and Molecular Structure: Diatomic Molecules"; Kronig, "The Optical Basis of the Theory of Valency."

0, 1, 2, 3, etc., respectively. If, for example, n were 2, then l could be 0 or 1, and the electron would be designated as $2s$ or $2p$, respectively. The number of electrons in an atom having the same values of n and l is indicated by a superscript; thus, $2p^4$ would mean that in the given atom there are four $2p$ electrons, that is, four electrons for which $n = 2$ and $l = 1$. The question of the number of electrons in an atom that can have the same values of both n and l will be considered shortly.

1b. Magnetic and Spin Quantum Numbers.—In a magnetic field the vector representing the orbital angular momentum undergoes a precessional motion, describing the surface of a cone whose axis is the direction of the field. The possible orientations of the vector in space are limited by the necessity, according to quantum theory, that the component of the angular momentum in the field direction shall be determined by an integral quantum number. In other words, there is space quantization of the angular momentum in an electric or magnetic field, and the component in the direction of the field is represented by a quantum number; this is called the *magnetic quantum number* of the electron, and is designated by the symbol m_l . The maximum value of m_l is clearly l , and its minimum is zero; the possible values are consequently given by

$$m_l = l, l - 1, \dots, 0, \dots, -(l - 1), -l \quad (1.1)$$

The negative values of m_l take into account the fact that the component of the angular momentum vector may point in a direction opposite to that of the magnetic field (Fig. 1). There are evidently $2l + 1$ possible orientations in space of the angular momentum vector of the electron, each different orientation being represented by a different value of the quantum number m_l . Even in the absence of a magnetic field, this number retains a definite significance in providing a description of the electron. For zero field, however, the value of m_l has no effect on the binding energy of the electron.

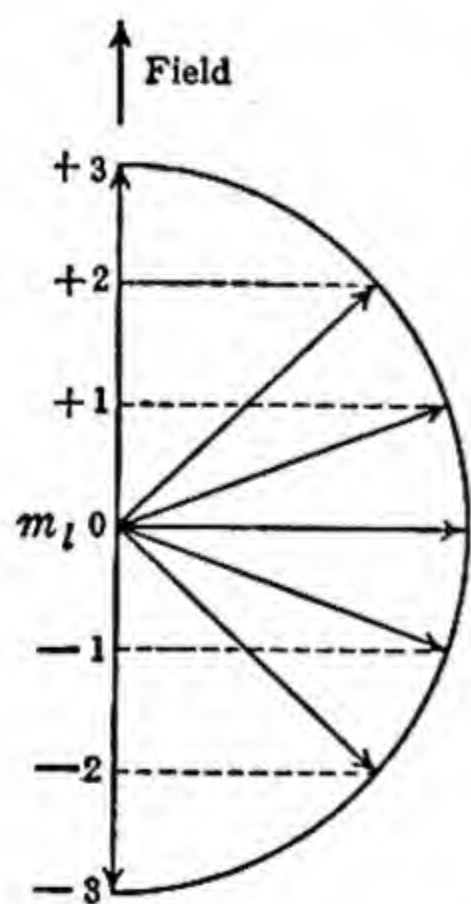


FIG. 1. Space quantization in magnetic field

In order to account for the fine structure of the lines in the spectra of certain atoms, it was found necessary to postulate that an electron has an angular momentum of rotation about its own axis. That is to say, every electron must be regarded as possessing *spin angular momentum*; the magnitude of this momentum is given by the expression $\sqrt{s(s + 1)}h/2\pi$, where s can only have the value of $\frac{1}{2}$. In a magnetic field the vector representing the spin momentum can orient itself so that its component is either in the direction

of the field or opposite to it; the corresponding spin quantum numbers m_s are then $+\frac{1}{2}$ or $-\frac{1}{2}$.

1c. The Pauli Exclusion Principle.—According to the foregoing discussion the state of an electron can be determined by four quantum numbers, namely n , l , m_l and m_s ; the possible values of l and m_l depend on n , while m_s can be either $+\frac{1}{2}$ or $-\frac{1}{2}$. A further restriction is placed on the values of these quantum numbers by the *Pauli exclusion principle*, which states that two electrons in the same atom cannot have all four quantum numbers identical. The operation of this principle can be readily understood by considering some particular cases. If the principal quantum number n is unity, the azimuthal quantum number l can only be zero; consequently m_l must be zero. If two electrons for which $n = 1$ are under consideration, three of the four quantum numbers must be identical, i.e., $n = 1$, $l = 0$, $m_l = 0$ for both; hence the fourth, m_s , must differ for the two electrons if the Pauli principle is to be obeyed. The only possible values of m_s are $+\frac{1}{2}$ and $-\frac{1}{2}$, and so it is obvious that in any atom there can never be more than two electrons in the K shell, i.e., with $n = 1$. The four quantum numbers of these two electrons are as follows:

n	l	m_l	m_s	Symbol
1	0	0	$+\frac{1}{2}$	$1s$
1	0	0	$-\frac{1}{2}$	$1s$

Both these electrons would be represented by the symbol $1s$, and so an atom cannot possess more than two $1s$ electrons; thus, $1s^2$ represents a complete shell.

If the principal quantum number is 2, l may be 1 or 0. When $l = 1$, the possible values of m_l are 1, 0 and -1 , so that there are three different assignments for the three quantum numbers. In addition, when $l = 0$, the value of m_l must also be 0, and this makes a fourth arrangement that is different from the other three. In each case, m_s may be $+\frac{1}{2}$ or $-\frac{1}{2}$, and so there are eight ways, and no more, in which the four quantum numbers may be assigned when n is 2. The quantum numbers of the eight electrons which may have the principal quantum number of 2 are given below.

n	l	m_l	m_s	Symbol
2	0	0	$+\frac{1}{2}$	$2s$
2	0	0	$-\frac{1}{2}$	$2s$
2	1	1	$+\frac{1}{2}$	$2p$
2	1	1	$-\frac{1}{2}$	$2p$
2	1	0	$+\frac{1}{2}$	$2p$
2	1	0	$-\frac{1}{2}$	$2p$
2	1	-1	$+\frac{1}{2}$	$2p$
2	1	-1	$-\frac{1}{2}$	$2p$

The symbols for these electrons are $2s$, when $n = 2$ and $l = 0$, and $2p$ when $n = 2$ and $l = 1$.

It was seen above that there are $2l + 1$ values of m_l for every value of l , and there are n possible values of l , viz., $n - 1, n - 2, \dots, 0$; the maximum

number of assignments for the four quantum numbers, allowing for the fact that m_l can have two values, is then given by the summation

$$\sum_{l=0}^{n-1} 2(2l + 1) = 2n^2. \quad (1.2)$$

The maximum number of electrons in any atom having the principal quantum number n is thus seen to be $2n^2$.

From general considerations, which are borne out by an examination of the tables of quantum number assignments given above, it is evident that for any value of n , there can be no more than two electrons for which l is zero. That is to say, for each value of the principal quantum number n there can be only two s electrons. There is thus a maximum number of two $1s$ electrons, two $2s$ electrons, two $3s$ electrons, and so on. When any group of electrons contains its maximum number, it is said to be a completed group or closed shell; consequently, $1s^2$, $2s^2$, $3s^2$, etc., represent closed shells of electrons.

When n is greater than unity, l may have the value unity as well as zero, and the maximum number of p electrons, i.e., electrons for which $l = 1$, is equal to six. It follows, therefore, that $2p^6$, $3p^6$, $4p^6$, and so on, would indicate closed shells of p electrons. Since there can be no p electrons when n is unity there are, of course, no $1p$ electrons. When n is 3 the value of l may be as high as 2, and then d electrons become possible. By the use of arguments similar to those presented above, it can be readily shown that the maximum possible number of d electrons for any value of n is ten; hence $3d^{10}$, $4d^{10}$, etc., would imply closed shells of d electrons. In general there are $2(2l + 1)$ electrons in any completed group; $2l + 1$ gives the number of values of m_l for a given l , and the factor 2 arises because m_l can be $+\frac{1}{2}$ or $-\frac{1}{2}$.

If the principal quantum number $n = 1$, there can be only s electrons, as already seen; when $n = 2$, both s and p electrons are possible; for $n = 3$, there can be s , p and d electrons, and so on. It follows, therefore, that the completed K , L , M and N shells, i.e., $n = 1, 2, 3$ and 4 , respectively, of an atom could be represented symbolically in the following manner.

K shell	$1s^2$	Total = 2
L shell	$2s^2 2p^6$	= 8
M shell	$3s^2 3p^6 3d^{10}$	= 18
N shell	$4s^2 4p^6 4d^{10} 4f^{14}$	= 32

The totals, 2, 8, 18 and 32, respectively, represent the maximum numbers of electrons that can occupy the first four principal quantum levels. In agreement with equation (1.2), these totals are equal to $2n^2$ in each case.

1d. Electronic Configurations.—In the study of the arrangement of the electrons in any atom, it is imagined that a hypothetical process is carried out. Starting with the bare nucleus, it is supposed that the electrons, equal in number to the nuclear charge, are added one by one until the neutral

atom is obtained. By making use of a variety of information, most frequently obtained from optical and X-ray spectra of the atom concerned, it is possible to determine the arrangement of the electrons in the various groups and subgroups. The complicated procedure is greatly simplified by assuming, what appears to be the case for most atoms, that the main structural arrangement of electrons in any atom is the same as in the preceding one. It is then usually sufficient to determine the position occupied by the one additional electron which distinguishes the two atoms. The principle upon which the elucidation of electronic configuration is based is, that in passing from any element to the one with the next higher atomic number, the additional electron occupies the place in which it becomes most firmly bound.

The detailed results of this method of studying atomic architecture need not be given here,² but reference may be made to a few cases. The hydrogen atom, for example, has one electron only, and this must undoubtedly be $1s$, since the binding energy of an electron in the K shell, ($n = 1$) is always greater than for one in the L shell ($n = 2$). The next atom, helium, with two electrons must consequently have the configuration $1s^2$. The K shell is now complete and so the third electron, in the lithium atom, must enter the L shell; the distribution of the three electrons will then be according to the representation $1s^2 2s$. When the $2s$ subgroup is filled with two electrons, as in beryllium, the next electron will enter the $2p$ group, giving $1s^2 2s^2 2p$ as in boron, and so forth.

Attention should be called at this point to the necessity of distinguishing between an atom in its normal, or ground, state and the atom in an electronically excited or metastable state. One of the latter states results when an atom takes up sufficient energy for one or more of its electrons to be changed to a quantum level in which the binding energy is less than in the normal state. The change may take place in any or all of the four quantum numbers at the same time. Generally, changes in the principal quantum number are associated with the largest excitation energies. The formation of electronic states that differ from the ground state may be illustrated with reference to the element carbon. This atom has six electrons, and the arrangement giving the strongest binding is $1s^2 2s^2 2p^2$; hence, this symbol presumably represents the electronic configuration of the normal, or lowest, state of the carbon atom. However, it will be seen later that there are three different ways of distributing the two $2p$ electrons among the quantum numbers m_l and m_s . Hence there are actually three electronic states of atomic carbon whose energies are close together. The most stable state, with the lowest energy, is the ground state, and the other two states, referred to as *metastable states*, have slightly higher energies. In addition to these three states, in which the electrons have the same values of n and l , there are other states, the *excited states*, in which either or both of these quantum numbers is changed for one of the electrons. The first excited state of carbon, for example, is $1s^2 2s 2p^3$, in which one of the $2s$ electrons has been raised to the $2p$ level.

² Glasstone, "Text-Book of Physical Chemistry," p. 83 et seq.

1e. Russell-Saunders Coupling.—In the characterization of the electronic configuration of an atom, the type of representation given above, which is based on n and l values only, is insufficient and further information is desirable. This fact is brought out by the existence of the three states of the carbon atom, all of which are represented by $1s^2 2s^2 2p^2$, as mentioned in the preceding paragraph. For most atoms it is satisfactory to assume the existence of *Russell-Saunders coupling*, also referred to as *LS coupling*. This type of behavior implies that the orbital angular momenta of all the electrons in the atom are strongly coupled together to give a resultant momentum, indicated by the quantum number L , and that similarly the spins are coupled to give the resultant quantum number S . The possible values of L are determined by the different ways in which the l values for the individual electrons can be added vectorially with the restriction, according to the quantum theory, that the resultant momentum must be zero or integral. For an atom containing a large number of electrons the determination of the permitted L values is simplified by the fact that closed shells, such as s^2 , p^6 , d^{10} , and so on, give a resultant orbital angular momentum of zero. For a single electron outside closed shells, L is of course equal to l for that electron, and for a pair of electrons having individual azimuthal quantum numbers l_1 and l_2 , the possible values of the resultant L are given by

$$L = l_1 + l_2, l_1 + l_2 - 1, l_1 + l_2 - 2, \dots, l_1 - l_2, \quad (1.3)$$

assuming l_1 is greater than l_2 . The L values for three electrons are obtained by finding those for two of them, as just described, and then adding vectorially the l for the third electron, with the usual restriction as to the resultant being zero or integral. In general, for more than two electrons lying outside closed shells, the procedure is to determine the resultant momentum for each shell, e.g., L_1 and L_2 , and then to combine them vectorially, so that

$$L = L_1 + L_2, L_1 + L_2 - 1, \dots, L_1 - L_2, \quad (1.4)$$

where $L_1 > L_2$. To take a simple illustration, suppose there are three electrons with the configuration sp^2 ; for the one s electron, L must be equal to l , and hence it is zero. For the two p electrons, the l values, i.e., l_1 and l_2 , are both unity and so, by equation (1.3), the resultant momentum L has the possible values 2, 1 and 0. If these are taken as L_1 , and L_2 is the value for the one s electron, i.e., zero, it follows from equation (1.4) that the quantum number for the resultant orbital momentum of the three electrons is

$$L = 2, 1, 0.$$

The resultant spin quantum number S for all the electrons in an atom is the absolute value, i.e., exclusive of sign, obtained by algebraic addition of the m_s values for the several electrons. The determination of S is very simple, partly because closed shells make no contribution to the resultant, and partly because m_s can be either $+\frac{1}{2}$ or $-\frac{1}{2}$ only. For one electron S

must be $\frac{1}{2}$, while for two electrons it may be 1 or 0, according as the individual spins are in the same direction, i.e., $+\frac{1}{2}$ and $+\frac{1}{2}$ (or $-\frac{1}{2}$ and $-\frac{1}{2}$), or in opposite directions, i.e., $+\frac{1}{2}$ and $-\frac{1}{2}$. For three electrons, the possible S values are $\frac{3}{2}$ and $\frac{1}{2}$; the former occurs when all the spins are in the same direction, that is, they are all three $+\frac{1}{2}$ or $-\frac{1}{2}$, and the latter arises when two spins are in one direction and the third spin is in the other direction. It will be evident that when an atom contains an even number of electrons the resultant spin quantum number S must be zero or integral; if there are an odd number of electrons S will be equal to an odd number of half integers.

If. Multiplet States.—In Russell-Saunders (LS) coupling, the L and S values for an atom are coupled vectorially to give the quantum numbers J for the *total angular momentum* of all the electrons. From the general rule for the quantum addition of vectors, it follows that the possible values of J are given by

$$J = L + S, L + S - 1, L + S - 2, \dots, |L - S + 1|, |L - S|; \quad (1.5)$$

the symbols $|L - S|$, etc., indicating absolute values, imply that J is always positive. Because the orbital angular momenta of the various electrons are strongly coupled together, and the spin angular momenta are also strongly coupled, terms with different L values or different S values have appreciably different energies. On the other hand, the various J values, resulting from the vectorial combination of L and S , correspond to states that have energies that are generally relatively close together. An atomic state with given L and S thus consists of a group of components having energies which do not differ appreciably; the number of components of the group is equal to the number of possible J values. The particular state is then said to be a *multiplet* and to have a *multiplicity* equal to the number of J values. Suppose, for example, that S is $\frac{1}{2}$, then

$$J = L + \frac{1}{2}, L - \frac{1}{2},$$

so that the multiplicity is two. If S is 1, then

$$J = L + 1, L, L - 1,$$

the multiplicity then being three. In general, it can be seen that provided L is greater than S , the number of J values, which gives the multiplicity of the given atomic state, is equal to $2S + 1$. It will be noted, in view of what was said above concerning S , that the multiplicity will be odd if the atom contains an even number of electrons, but it will be even if the number of electrons is odd. In the event that L is less than S , there is only one possible J value, although $2S + 1$ may be greater than unity. For example, if an atom contains one s electron outside closed shells, L is zero and S is $\frac{1}{2}$, so that J can only be $\frac{1}{2}$; the state is thus a singlet, that is, the multiplicity is unity, although in this case $2S + 1$ is equal to two. States of this kind are frequently regarded as possessing a hypothetical multiplicity of two, both components possessing identical energies.

1g. Term Symbols.—Just as the letters s , p , d and f are used to represent l values of 0, 1, 2 and 3, respectively, for single electrons, so the corresponding capitals S , P , D and F are employed to indicate L values of 0, 1, 2 and 3, respectively, for all the electrons in a given atom. The letter, referred to as the *term letter*, is preceded by a superscript representing the multiplicity of the state, equal to $2S + 1$, and frequently it is followed by a subscript giving the J value. Suppose, for the purpose of illustration, that the resultant orbital quantum number L of the electrons in an atom is 2, and that the resultant spin S is 1; the *term symbol* for the particular atom will be 3D , since $2S + 1$ is equal to 3. The possible J values are 3, 2 and 1, so that the complete symbols for the three states of the triplet would be 3D_3 , 3D_2 and 3D_1 . In some cases it is convenient to distinguish atom terms that are *even* or *odd*, according as the numerical sum of the l values for all the electrons in the atom is even or odd. The corresponding symbols are g for *gerade* (even) and u for *ungerade* (odd), and these are used as subscripts in place of the J value; thus, 3D_g would represent an atomic state in which the sum of the l values for all the electrons is even.

A further form of characterization of multiplet atomic states is sometimes convenient. As a general rule, the state with the lowest J value of the multiplet has the lowest energy, that is, it is the most stable, and the energy increases as J is increased. Such a state would be regarded as a normal multiplet. However, sometimes the reverse is true, the lowest J value corresponding to the highest energy, and vice versa. In this case the multiplet is said to be *inverted*. The halogens, for example, in their lowest states, are doublets whose term symbols are ${}^2P_{3/2}$ and ${}^2P_{1/2}$; since the former is the more stable state, i.e., the usual ground state, the doublets are inverted.

1h. Permitted Atomic States.—The essential importance of the term symbol lies in the fact that in a large number of cases it can be determined from a study of the atomic spectrum, and from a knowledge of this symbol information can be obtained concerning the electronic configuration of the atom. Consider an atom having six electrons designated by $1s^2 2s^2 2p^2$. The $1s^2$ and $2s^2$ electrons constitute closed shells, and so L and S are determined by the two p electrons. Since l for each of these is unity, it follows that for the atom may be 2, 1 or 0, representing D , P and S states, respectively. For the two electrons S may be 1 or 0, corresponding to multiplicities of 3 and 1, respectively. The theoretical terms for the atom under consideration are thus 3D , 3P , 3S , 1D , 1P and 1S ; however, it is found by means of quantum mechanics that of these states 3P , 1D and 1S are the only ones possible, the others being forbidden. In general, any atom having two p electrons outside closed shells should, theoretically, give rise to the same three terms. By working in an analogous manner the possible states for various numbers of equivalent electrons, that is, of electrons with the same n and l values, have been determined. An atom consisting of closed shells only, i.e., s^2 , p^6 , d^{10} , etc., is always in a 1S state; the permitted terms for certain other cases are given in Table I. If there are two or more d electrons, the number of terms becomes large, and includes F , G , etc., states, with L equal to 4, 5, etc. I⁴

will be observed that one p electron and five equivalent p electrons outside closed shells give the same atomic states. Similarly, two and four equivalent p electrons yield identical states. For obvious reasons, a single s , p or d electron will result in the formation of a 2S , 2P or 2D state, respectively.

Certain rules have been developed for determining which of a number of states that may result from the same electronic configuration is the *deepest*, that is to say, which state has the lowest energy and hence represents the

TABLE I. PERMITTED ATOMIC STATES FOR EQUIVALENT ELECTRONS

Electrons	Permitted States		
	2S	2P	2D
s	2S		
p		2P	
p^2	1S	3P	1D
p^3	4S	2P	2D
p^4	1S	3P	1D
p^5		2P	
d			2D

most stable (ground) state of the atom. In general, this state is the one with the highest multiplicity and the largest L value. For the case in which the electrons outside closed shells are represented by p^2 and p^4 , the lowest term should be 3P , followed by the possible term 1D and then by 1S . For three equivalent p electrons, i.e., p^3 , outside closed shells, the corresponding order would be 4S , 2D and 2P .

The application of these rules may be illustrated by means of a few simple cases. The ground term as derived from the spectrum of atomic carbon is 3P , and so its electronic structure, apart from closed shells, is apparently p^2 or p^4 . The carbon atom has six electrons of which two are undoubtedly of the $1s$ type, and hence the configuration would be either $1s^2 2s^2 2p^2$ or $1s^2 2p^4$. Of these alternatives the former is much more probable, for it is unlikely that there will be four $2p$ electrons while the $2s$ group remains vacant. This view is supported by the fact that the ground terms of the two preceding atoms, beryllium and boron, are 1S and 2P , respectively, in their normal states, corresponding to the structures $1s 2s^2$ and $1s^2 2s^2 2p$, respectively. Further confirmation is supplied by the 4S ground state of atomic nitrogen, which must consequently be represented by $1s^2 2s^2 2p^3$. It is of interest to recall, as mentioned in Section 1d, that there is evidence for the existence above the 3P ground state of carbon of two metastable states, namely, 1D and 1S , the former being the lower. This observation is in harmony with expectation, for it is seen from Table I that a p^2 configuration should be able to give rise to these three states, the energies increasing in the order 3P , 1D and 1S . In each of these states the electronic configuration of the carbon atom, so far as the quantum numbers n and l are concerned, is the same, namely $1s^2 2s^2 2p^2$, but there are differences in the values of m_l and m_s for the two $2p$ electrons. In the same connection, mention may be made of the metastable 2D and 2P states of atomic nitrogen, and of the metastable 1D and 1S states of oxygen.

In addition to the atomic carbon terms to which reference has just been made, there is spectroscopic evidence of a 5S term which undoubtedly represents an excited state. Since the 5S symbol does not appear in Table I, it must be concluded that this state does not arise from equivalent electrons. Such a condition can be explained by supposing that one of the $2s$ electrons has been raised to the $2p$ level, so that the electronic configuration is $1s^2 2s 2p^3$. There are, consequently, one s and three equivalent p electrons outside closed shells, and the atom term is now dependent on four nonequivalent electrons. In a case of this kind the procedure is to find first the terms that are possible for the three equivalent p electrons; these are, according to Table I, 4S , 2D and 2P . For the 4S state, which should be the one of lowest energy, the corresponding L and S values, referred to as L_1 and S_1 , are 0 and $\frac{3}{2}$, respectively. These L and S values must now be combined with the corresponding resultant quantum numbers for the other equivalent electrons. In the case under consideration there is only one s electron, for which L is also 0 and S is $\frac{1}{2}$; these are regarded as L_2 and S_2 , respectively. Thus,

$$\begin{array}{ll} L_1 = 0 & S_1 = \frac{3}{2}, \\ L_2 = 0 & S_2 = \frac{1}{2}, \end{array}$$

and the possible L and S values resulting from the combination of L_1 and L_2 , and of S_1 and S_2 , respectively, are

$$L = L_1 + L_2 = 0$$

and

$$S = S_1 + S_2, S_1 - S_2 = 2, 1.$$

Since L is zero, the combination must result in an S term; the possible multiplicities, $2S + 1$, are 5 and 3, so that the two states 5S and 3S are indicated, theoretically. The former of these might be expected to be the deepest; this is in agreement with experimental observation, and hence the results support the suggested structure $1s^2 2s 2p^3$ for the first excited state of atomic carbon. By combining the L and S values for the s electrons with those corresponding to the two other possible states for the equivalent p^3 electrons, i.e., 2D and 2P , other terms are obtained. None of these, however, has such a high multiplicity as the 5S term. It would not be surprising, of course, if some of these were found to occur as metastable excited states.

MOLECULAR QUANTUM NUMBERS

2a. Orbital Angular Quantum Number.—Sufficient has been stated here concerning electronic configurations and term symbols of atoms to permit the extension of the concepts to the study of molecules. The discussion will be restricted to diatomic molecules, for the results become very complicated when polyatomic molecules are considered. As a consequence of the strong electric field existing between the nuclei of a diatomic molecule, the resultant vector representing the angular momentum of all the electrons undergoes a precession about the field direction, which in this case is the internuclear axis

of the molecule. The situation is quite analogous to that referred to in connection with an atom in a magnetic or electric field (Section 1b). There is a corresponding space quantization of the orbital angular momentum vector, with the restriction that the quantum number of the component along the internuclear axis shall be zero or integral. This quantum number is given the symbol Λ and its possible values, $L + 1$ in all, are represented by

$$\Lambda = L, L - 1, L - 2, \dots, 2, 1, 0, \quad (2.1)$$

where L is the quantum number for the resultant orbital angular momentum for all the electrons in the molecule. The corresponding negative values, which appear in the equivalent expression for m_l for an atom in a magnetic field [equation (1.1)], do not occur here because in the electric field of the nuclei the energy of the electron is the same irrespective of the direction of its orbital motion. In other words, whereas $m_l = +l$ and $m_l = -l$ correspond to states with somewhat different energies, $\Lambda = +L$ and $\Lambda = -L$ represent states with identical energies. It is seen, therefore, that for each value of the resultant electronic orbital angular momentum L there are $L + 1$ possible molecular energy states, corresponding to the $L + 1$ values of the quantum number Λ . However, except when Λ is zero, all these states are *doubly degenerate* (see Section 6), for, as just seen, they are each made up of the two states, $\Lambda = +L$ and $\Lambda = -L$, having the same energies.

2b. Spin Quantum Numbers.—Just as electron spin is used to account for the multiplet structure of lines in the spectra of atoms, so the resultant spin of all the electrons is employed in connection with molecular spectra and the description of molecular states. The corresponding quantum number S is obtained in the usual manner by adding the spins of the various electrons outside closed shells; as for atoms, S is zero or integral if the total number of electrons is even, whereas it is an odd number of half integers if there is an odd number of electrons in the molecule. In the study of molecules, however, a complication arises because, with the exception of states for which Λ is zero, the orbital motion of the electrons produces a magnetic field in the direction of the nuclear axis. As a result, there is a precession of the vector representing the resultant spin S ; the components in the field direction, indicated by the quantum number Σ , are given in the familiar manner by the expression

$$\Sigma = S, S - 1, S - 2, \dots, 0, \dots, -(S - 1), -S. \quad (2.2)$$

Both positive and negative signs are included for opposite directions of spin in the magnetic field. There are thus $2S + 1$ different values of Σ for every value of S , and the corresponding molecular term will have a multiplicity of $2S + 1$. It should be emphasized that these arguments apply only if Λ is not zero; in the event that Λ is zero, the quantum number Σ has no significance, and the state is a singlet. Nevertheless, as is the case with atoms, the quantity $2S + 1$ is referred to as the multiplicity of any state, irrespective of the value of Λ ; the limitation must, however, be borne in mind.

2c. Coupling of Momenta.—As already seen, in atoms which exhibit LS coupling, the orbital angular momenta of the electrons are strongly coupled among themselves, and so also are the spin momenta; the two resultant vectors then combine to give the total electronic angular momentum. A similar type of behavior is postulated for molecules, the orbital and spin momenta combining to give the component of the total angular momentum along the internuclear axis. Since Λ and Σ are already the quantum numbers for the individual components of orbital momentum and spin, respectively, the resultant quantum number Ω for the component of the total momentum is obtained by algebraic, rather than vectorial, addition of Λ and Σ ; thus,

$$\Omega = |\Lambda + \Sigma|, \quad (2.3)$$

positive values only having significance. If Λ is not zero, there are $2S + 1$ possible values of Σ , as seen above; hence, for a given value of Λ other than zero, there are $2S + 1$ different values of Ω . These correspond to slightly different energies of the state having a particular L and S ; this state has, consequently, a multiplicity of $2S + 1$, as already noted. Since the quantum number Ω for a molecule corresponds to J for an atom, the descriptions *normal* and *inverted*, as applied to multiplets of a molecule, are used in the same sense as for an atom; a normal state is one in which the lowest energy level has the lowest Ω value, whereas in an inverted state the most stable level corresponds to the highest Ω value.

2d. Molecular Term Symbols.—Symbols are employed for the identification of molecular terms that are similar to those described for atoms (Section 1g). The Greek capitals Σ , Π , Δ , Φ , etc., are used to represent Λ values of 0, 1, 2, 3, etc.; the multiplicity $2S + 1$ is added as a superscript preceding the term symbol, while the Ω value is sometimes included as a following subscript. Thus, if for a given state $\Lambda = 2$, and $S = 1$, it would be represented by the symbol ${}^3\Delta$. Since Σ might be 1, 0, -1 , the quantum number Ω could be 3, 2, 1, so that the three levels of the triplet would be designated ${}^3\Delta_3$, ${}^3\Delta_2$ and ${}^3\Delta_1$, respectively.

Many stable diatomic molecules have completed electron shells only, and so L and hence Λ are zero; they have therefore Σ ground states. For odd-electron molecules, such as NO and HgH, and radicals, such as CN and OH, the value of Λ is generally not zero. For such substances Π and Δ states are most common. These terms are also found for the excited states of diatomic molecules that are normally stable. In the great majority of cases the observed multiplicities are either 1, 2 or 3; higher multiplets in molecular terms are rare. If the multiplicity $2S + 1$ is unity, then S must be zero, and in this case Ω is equal to Λ . If the multiplicity is two, then S is $\frac{1}{2}$, and the values of Ω are $\Lambda + \frac{1}{2}$ and $\Lambda - \frac{1}{2}$; finally, when the multiplicity is three, S must be unity, and the possible values of Ω are $\Lambda + 1$, Λ and $\Lambda - 1$.

2e. Symmetry Properties.—In addition to the quantum numbers Λ , Σ and Ω , derived from L and S , the *symmetry properties* of the electronic eigenfunctions (see Chapter II) are important in the identification of molecular

states. These symmetry properties of the eigenfunctions, which follow from wave mechanical considerations, are in certain cases related to the symmetry properties of the molecule as a whole. It will be seen in Section 31a that for a diatomic molecule, or for a linear polyatomic molecule, in a Σ state, reflection at any plane passing through the nuclei (or, what comes to the same thing in these cases, reflection through the origin, i.e., *inversion*, of both electrons and nuclei) the electronic eigenfunction either remains unaltered or else it merely changes sign. If the eigenfunction is unchanged then the state is referred to as a Σ^+ state, but if the sign is reversed it is designated a Σ^- state.

When the two nuclei of a diatomic molecule have the same charge, although not necessarily the same mass, e.g., $^{16}\text{O}^{16}\text{O}$ and $^{16}\text{O}^{18}\text{O}$, the electric field in which the electrons move has a center of symmetry at a point equidistant between the two nuclei. As a result of the reflection of the coordinates of all the electrons at this center of symmetry, that is, as a result of inversion, the electronic eigenfunction is either unaltered or merely changes sign (see Section 31b). If there is no change in the eigenfunction, the state is said to be *even* and is designated by the symbol g , while states for which the sign changes are referred to as *odd* and are characterized by the letter u , added as a subscript. Examples are Σ_g , Σ_u , Π_g , Π_u , Δ_g and Δ_u , the odd and even character not being restricted to any particular type of state, provided the two nuclei of the molecule have the same charge, i.e., they are identical or isotopic. All the levels of a given multiplet have the same g or u character; thus, the ground state of the C_2 molecule is a $^3\Pi_u$ term, all three constituents of the triplet being odd (u) states. It may be mentioned that even if the nuclei have charges which differ only slightly, as is the case with the CN radical, the electronic eigenfunctions possess g and u properties to some degree.

CHAPTER II

QUANTUM MECHANICS ¹

THE UNCERTAINTY PRINCIPLE

3a. Introduction.—According to classical mechanics it should be possible to determine precisely both the position and velocity, or momentum, of a moving particle. It has become apparent in recent years, however, that the classical point of view represents an approximation which is adequate for objects of appreciable size, but is quite unsatisfactory for describing the behavior of particles of atomic dimensions. It has been necessary, therefore, to devise a new mechanics for the treatment of electrons and atomic nuclei. In this new mechanics the exact position of a moving object, such as, for example, the orbit of an electron around the nucleus of an atom, is replaced by a function which determines the probability of the object being in the particular position. Because these probability functions satisfy differential equations which are analogous to those representing the variation of the amplitude of a wave, the new atomic mechanics has been referred to as the *wave mechanics*. Some writers, however, feel that the analogy may be misleading, and so the term *quantum mechanics* is generally used. It will be seen that the new approach to the study of small particles provides a satisfactory basis for many of the quantum postulates that had been previously applied, more or less empirically, to the treatment of atoms and molecules. Quantum mechanics has many achievements to its credit, but it is the purpose here to restrict attention to those aspects having direct chemical interest and which do not require advanced mathematical knowledge for their appreciation. Even with these severe limitations, it will be evident that quantum mechanics has made important contributions to the study of atoms and molecules that lie beyond the scope of classical mechanics.

3b. Waves and Particles: The Uncertainty Principle.—It is well known that the diffraction properties of light and other radiations, e.g., X-rays, can best be explained by the assumption that the radiations consist of a train of waves. On the other hand, an adequate interpretation of photoelectric phenomena and of the Compton effect necessitate the apparently contradictory postulate that the radiations are made up of a stream of particles (photons). Some clarification of the problem of wave-particle duality is possible by considering the respective conditions under which the wave and particle properties of radiation become evident. When light encounters a diffraction grating, so that interference phenomena occur, it is possible to determine the wave length of the light with an accuracy limited only by the

¹ Dushman, "The Elements of Quantum Mechanics"; Pauling and Wilson, "Introduction to Quantum Mechanics"; Tolman, "The Principles of Statistical Mechanics," Chapters VII and VIII.

precision of the measuring instruments. It will be seen shortly [equation (3.8)] that the wave length of a particular radiation may be regarded as being inversely proportional to the momentum of the equivalent photon, and so the diffraction experiments may be utilized to evaluate this momentum with a considerable degree of accuracy. However, if it is required to determine the position of a photon in the experiment, a fundamental difficulty immediately arises. The very fact that interference phenomena are observed means that it is not possible to state exactly the path of a particular photon as it passes through, or is reflected from, the diffraction grating. The definite pattern of light and dark rings, or spots, produced by the radiation implies that the position of a photon is determined by a *probability* relationship, but there is no *certainty* that a particular photon will be found in a particular place.

Turning now to phenomena such as the Compton effect, for an interpretation of which it is necessary to invoke the particle properties of radiation, it becomes possible to determine the position of the photon with considerable exactness, but now there is uncertainty as to its momentum. In the Compton experiment an X-ray photon strikes an electron, so that in a sense the position of the former may be identified with that of the electron. At the same time, however, the wave length of the scattered X-ray, and hence the momentum of the corresponding photon, is changed from its initial value. It is true that the change in wave length or momentum can be calculated from a knowledge of the angle between the incident and scattered beams of X-rays, but the distribution of the scattering angle is itself determined by a probability function and is consequently uncertain.

It is apparent, therefore, that in the experiments by means of which it is possible to obtain the momentum of a light photon with some accuracy, there is no certainty, only a probability, as to its position. On the other hand, when the position can be fixed exactly, the momentum is uncertain. This reciprocal relationship, concerning the inability to define precisely both position and momentum simultaneously, extends to electrons, and probably to particles of every type, as may be seen in the following manner. Suppose it is desired to determine the position of a particle; it may be illuminated by means of light of wave length λ , and then observed through the lens of a microscope. According to optical theory, the uncertainty Δx , in the x direction, in determining the position of the particle depends on the value of λ and on the angle θ , the aperture of the lens; thus,

$$\Delta x = \frac{\lambda}{\sin \theta}. \quad (3.1)$$

In order to determine the position accurately, therefore, the wave length λ of the light should be small, so that Δx is also small. Suppose the particle under observation is an electron; the "light" used would have to be short X-rays or γ -rays, and in these circumstances there would be a considerable Compton effect. As a result of the impact between the photon and the

electron, the former is scattered, as mentioned earlier, and the latter recoils so that its momentum is changed. As long as the scattering angle is within certain limits the photon will still enter the microscope lens and be visible. That is to say, there is a degree of uncertainty in the angle of scattering of the photon, and hence in the change of momentum of the electron, that is still visible in the microscope. This uncertainty of the momentum, in the x direction, is given, approximately, by

$$\Delta p_x = \frac{h}{\lambda} \sin \theta, \quad (3.2)$$

so that the product of the uncertainties of position and of momentum may be represented by

$$\Delta x \Delta p_x = h, \quad (3.3)$$

where h is the Planck (quantum theory) constant. Any attempt to improve the accuracy in the determination of the position of the electron, e.g., by decreasing the wave length of the light, will thus be offset by a loss of accuracy in assessing the momentum. On the other hand, if the conditions are such that the momentum can be evaluated with some degree of precision, there will be increased uncertainty concerning the position of the electron.

The foregoing conclusions have been generalized by Heisenberg (1927) in the form of the *uncertainty principle*; this is regarded as a fundamental law of nature applicable to all particles. If p and q represent two conjugate variables, such as momentum and position of any particle, the product of the uncertainties Δp and Δq in the determination of their respective values is approximately equal to the Planck constant; thus

$$\Delta p \Delta q \approx h. \quad (3.4)$$

The fundamental cause of this uncertainty lies in the fact that the particle under observation interacts with the measuring system. In the determination of the position of an object, for example, a beam of light is directed upon it; as a result, however, the object suffers a recoil which alters its momentum. If the particle under consideration is macroscopic in size, the magnitude of the uncertainty is negligible in comparison with the normal experimental error, and so the effect of the Heisenberg principle is of no significance. For such particles, therefore, classical mechanics may be employed without any detectable discrepancies. When the particles under observation are small, for example, electrons and nuclei, the uncertainty in the determination of position and momentum is of sufficient significance to render classical mechanics invalid. The old mechanics, implying the precise identification of the conjugate variables, p and q , must therefore give way to the new system in which exact values are replaced by probabilities.

3c. The de Broglie Relationship.—Although the dual wave and particle aspects of radiation appear at first sight to be mutually exclusive, they may perhaps better be considered as complementary. In certain experiments the

particle property is evident, while in others the wave property becomes apparent. The situation may be summed up in the postulate that radiations consist of particles, or photons, whose movements are influenced by waves, or, in more general terms, whose distribution in space, or the probability of being found at a given point, satisfies an equation of the form representing the propagation of waves. By the use of relatively simple arguments it is possible to derive a relationship between the particle properties, such as the momentum, and the wave properties, such as the equivalent wave length. According to the quantum theory of radiation, the energy of a photon is equal to $h\nu$, where ν is the frequency of the particular radiation; if this value of the energy is equated to that given by the relativity relationship between energy and mass, it follows that

$$h\nu = mc^2, \quad (3.5)$$

where m is the mass of the photon and c is the velocity of light. If λ is the wave length of the radiation, then

$$\lambda = \frac{c}{\nu}, \quad (3.6)$$

and combination with equation (3.5) leads to the result

$$\lambda = \frac{h}{mc}. \quad (3.7)$$

Since mc is equal to the momentum of the photon, which may be represented by the symbol p , it follows that

$$\lambda = \frac{h}{p}. \quad (3.8)$$

The dualism of the wave and particle functions of radiation led de Broglie (1925) to suggest that a similar dualism might exist for electrons and other material particles. He suggested that such particles might be associated with *matter waves*, the wave length of which was related to the momentum by equation (3.8). It was pointed out shortly afterwards, by Elsasser (1925), that evidence for the wave nature of electrons might be obtained by observing diffraction effects under suitable conditions. Such observations were actually made by Davisson and Germer (1927), who studied the diffraction of electrons from the surface of a nickel crystal, and, independently, by Thomson (1927), who used extremely thin films of metal as diffraction gratings. In each case the results were in satisfactory agreement with those to be expected from waves whose lengths were equal to the values calculated from the known momenta by means of the de Broglie relationship [equation (3.8)]. Further confirmation of the idea of the association of waves and matter has been provided by the diffraction phenomena observed with particles of hydrogen and helium. Theoretically, such effects should exist for all particles, but when the masses are relatively high the equivalent wave lengths are too small for suitable diffraction gratings to be possible.

THE SCHRÖDINGER EQUATION

4a. The Wave Equation.—In developing the equations, or laws, of quantum mechanics it must be realized at the outset that it is necessary to make certain postulates. There is no absolute proof of these postulates, but they find support in the fact that they lead to conclusions that are in harmony with observation. It must be pointed out, however, that this agreement with experiment is no proof of the validity of the particular postulates, neither does it imply that they have any definite physical significance. It will be seen that the fundamental equation of quantum mechanics may be obtained on the basis of two entirely different sets of postulates.

In the derivation of the so-called *wave equation*, Schrödinger² made use of the de Broglie relationship between the momentum of a particle and the wave length of the associated matter waves. This, in fact, represents the essential postulatory basis of Schrodinger's approach to the new mechanics. In order to follow the development, it is convenient to consider, in the first place, the simplest type of wave motion, namely the vibrations of a stretched string. If w is the amplitude of vibration at any point whose coordinate is x , at a time t , then the appropriate partial differential equation for the wave motion is

$$\frac{\partial^2 w}{\partial x^2} = \frac{1}{u^2} \cdot \frac{\partial^2 w}{\partial t^2}, \quad (4.1)$$

where u is the velocity of propagation of the waves, sometimes called the *phase velocity*. Provided u is constant, as it probably is, it is possible to solve equation (4.1) by the method of separating the variables; thus w may be expressed in the form

$$w = f(x)g(t), \quad (4.2)$$

in which $f(x)$ is a function of the coordinate x only, while $g(t)$ is a function of the time t only. For the motion of standing waves, such as occur in a stretched string, it is known that $g(t)$ may be represented by

$$g(t) = A \sin 2\pi\nu t, \quad (4.3)$$

where ν is the vibration frequency, and A is a constant, the maximum amplitude. The equation for w may then be written as

$$w = f(x)A \sin 2\pi\nu t, \quad (4.4)$$

and hence

$$\frac{\partial^2 w}{\partial t^2} = -f(x)4\pi^2\nu^2(A \sin 2\pi\nu t) \quad (4.5)$$

$$= -4\pi^2\nu^2 f(x)g(t). \quad (4.6)$$

From equation (4.2) it follows that

$$\frac{\partial^2 w}{\partial x^2} = \frac{\partial^2 f(x)}{\partial x^2} g(t), \quad (4.7)$$

² Schrödinger, *Ann. Physik*, 79, 361, 489 (1926).

and combination of this result with equations (4.1) and (4.6) gives

$$\frac{\partial^2 f(x)}{\partial x^2} = -\frac{4\pi^2\nu^2}{u^2} f(x). \quad (4.8)$$

Further, the frequency of the vibrations ν and the velocity u are related by the equation $u = \lambda\nu$, where λ is the corresponding wave length; hence, equation (4.8) may be written as

$$\frac{\partial^2 f(x)}{\partial x^2} = -\frac{4\pi^2}{\lambda^2} f(x). \quad (4.9)$$

It will be noted that the time variable t has been eliminated from this equation, which consequently represents the variation of the amplitude function $f(x)$ with x at a definite instant.

4b. Eigenvalues and Eigenfunctions.—Attention may be called to certain other matters in connection with equation (4.9). It can be seen that the solutions $f(x)$ can have significance only for certain definite values of the wave length λ ; these are the wave lengths corresponding to the normal modes of vibration of the stretched string. The values are sometimes referred to as the *proper values* or *characteristic values*, but the hybrid term *eigenvalues* is most frequently used, especially in connection with the analogous quantities encountered in quantum mechanics. The corresponding functions $f(x)$, which are the solutions of equation (4.9), are called the *eigenfunctions* or *wave functions*. In order that they may be suitable, these functions must satisfy certain conditions which in the case under consideration are almost self evident. In the first place, $f(x)$ must be zero at each end of the string, since the system is fixed at these points, and the amplitude of vibration must then be zero. In the second place, $f(x)$ must be single valued and finite between the limits of x represented by the two ends of the string; in other words, at every point on the vibrating string the amplitude has a definite value at any given instant of time. The importance of these considerations relating to λ and $f(x)$ will be evident shortly in connection with the treatment of the fundamental equation of wave mechanics.

4c. The Schrödinger Equation.—The equation (4.9) for wave motion in one direction may be extended to movement in three dimensions, represented by the coordinates x , y and z . If $f(x)$ for one coordinate is replaced by $\psi(x, y, z)$, which is the amplitude function for three coordinates, equation (4.9) takes the form

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} = -\frac{4\pi^2}{\lambda^2} \psi, \quad (4.10)$$

where ψ has been written, for the sake of brevity, in place of $\psi(x, y, z)$. By making use of the symbol ∇^2 for the Laplacian operator, i.e.,

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}, \quad (4.11)$$

equation (4.10) can be written more concisely as

$$\nabla^2\psi = -\frac{4\pi^2}{\lambda^2}\psi. \quad (4.12)$$

The fundamental postulate of the Schrödinger method in quantum mechanics is that an equation of the form of (4.12) may be applied to all particles, including photons, electrons and atoms. Upon introducing, as a further postulate, the de Broglie relationship, equation (3.8), which gives the connection between the wave length and the momentum, equation (4.12) becomes

$$\nabla^2\psi = -\frac{4\pi^2 p^2}{h^2}\psi. \quad (4.13)$$

If $V(x, y, z)$ abbreviated to V , which is a function of position, is the potential energy of the particle, then its kinetic energy T is equal to $E - V$, where E is the total energy. Further, since the kinetic energy is equal to $\frac{1}{2}mv^2$ where m is the mass of the particle and v is its velocity, it follows that

$$T = E - V = \frac{1}{2}mv^2. \quad (4.14)$$

The momentum p is equal to mv , and so

$$E - V = \frac{p^2}{2m}. \quad (4.15)$$

Substituting this result for p^2 in equation (4.13) then leads to

$$\nabla^2\psi + \frac{8\pi^2 m}{h^2} (E - V)\psi = 0, \quad (4.17)$$

or

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{8\pi^2 m}{h^2} (E - V)\psi = 0. \quad (4.18)$$

Either of these equivalent expressions, equations (4.17) and (4.18), is the *wave equation* for a single particle; this was first derived by Schrödinger and applied by him to solve a number of problems in atomic physics.

4d. Behavior of Eigenfunctions.—Just as the amplitude functions $f(x)$ in the equation (4.9) for a vibrating string have significance only for certain definite values of the wave length λ , so the functions ψ are satisfactory solutions of equation (4.18) only for certain values—the eigenvalues—of the total energy E . For an atom, these eigenvalues are the equivalent of the discrete set of energy values postulated by the Bohr theory. The corresponding values of the function ψ are referred to as the wave functions, or eigenfunctions, of the Schrödinger equation. In order that these solutions of equation (4.18) may be satisfactory for the purpose of treating electrons, and other material particles, it is necessary to add a further postulate,

analogous to that already considered in connection with the amplitude functions for the case of a stretched string. The functions ψ must be single valued, continuous, and finite throughout the whole of the configuration space of the system under consideration, that is, for all possible values of the coordinates x , y and z , including infinity. Functions of this type have been called *well-behaved functions*, and consequently it is postulated that a satisfactory solution ψ of the wave equation must be a well-behaved function.

PROPERTIES OF EIGENFUNCTIONS

5a. Significance of the Wave Function.—In connection with the propagation of sound, and in Maxwell's electromagnetic theory of light, the square of the amplitude, as it appears in the appropriate wave equation, is proportional to the intensity of the sound, or the light, respectively. A somewhat analogous concept, modified by the requirements of the uncertainty principle, is made the basis of the postulate concerning the physical significance of the wave function, or eigenfunction, for a given system. The essential idea is that the probability of finding the system at a particular point in space is proportional to the square of the wave function at that point. However, in order to express this postulate in more precise mathematical form, it is necessary to develop certain ideas relative to the use of what are called "complex quantities."

In some circumstances the wave function ψ may include a term involving the imaginary quantity i , the square root of minus one, i.e., $i = \sqrt{-1}$. The value of ψ^2 may then be real or imaginary, depending on the nature of the expression for ψ . Since the probability of finding a material particle at a given point in space must always be real, it is defined in terms of the product $\psi\psi^*$, sometimes written as $|\psi|^2$, where ψ^* is the complex conjugate of ψ ; this product is always real, irrespective of whether ψ is real or imaginary.³ If a particular eigenfunction is real, and contains no imaginary terms, the function and its complex conjugate will be identical. Under these conditions, which are of frequent occurrence in connection with the wave functions employed in quantum mechanics, the product $\psi\psi^*$, which is related to the probability of finding the particle or system at a given point, is equal to ψ^2 .

Bearing in mind the foregoing considerations, the postulated definition of the wave function $\psi(x, y, z)$ of the three coordinates x , y and z , for a given system, such as one or more electrons, is that the quantity

$$\psi(x, y, z)\psi^*(x, y, z)dxdydz$$

³ The complex conjugate of any function is obtained by changing i , wherever it appears, into $-i$; thus the complex conjugate of e^{a+bi} is e^{a-bi} , and the product is the real quantity e^{2a} . Similarly, the complex conjugate of $a + bi$ is $a - bi$, and the product, $a^2 + b^2$, is real. The product of any function A and its complex conjugate, i.e., AA^* , is often written in the form $|A|^2$, where the symbol $|A|$ stands for the *modulus* or *absolute value* of A . Of course, if A contains no imaginary terms, A and A^* are identical, and $|A|^2$ is equal to A^2 .

is proportional to the probability of finding the particular system in the small volume element $dx dy dz$, situated at a point in space represented by the coordinates x, y, z . The expression given above is generally abbreviated to the form $\psi\psi^*d\tau$; this represents the probability that the system under consideration may be found in the small element $d\tau$ of the configuration space of the system. By the configuration space is meant the whole of the space in which the system may occur. This is not necessarily restricted to three coordinates; for if two independent particles, such as two electrons, are involved, there will be a total of six coordinates necessary to define the position of the system in the configuration space.

In view of the definition just given it is easy to understand why the product $\psi\psi^*$ is referred to as the *probability distribution function* for the configuration of the given system.

5b. Normalized and Orthogonal Eigenfunctions.—The integral of $\psi\psi^*d\tau$ over the whole of the configuration space is evidently proportional to the total probability of finding the system somewhere in space. This quantity must, of course, be finite, and it is for this reason that the eigenfunction ψ satisfying the Schrodinger wave equation has been postulated to be well-behaved, in the sense that it is finite, single valued, and continuous throughout the whole of the configuration space. For many purposes it is convenient to regard $\psi\psi^*d\tau$ as equal to, rather than as proportional to, the probability of finding the system at a given point in space. If this is the case, the integral over the whole of the configuration space, that is, from values of $-\infty$ to $+\infty$ of the coordinates, would of necessity be equal to unity, so that

$$\int_{-\infty}^{\infty} \psi\psi^*d\tau = 1. \quad (5.1)$$

An eigenfunction which satisfies an equation of this type is said to be *normalized to unity* or, in brief, *normalized*. Any solution of the wave equation may be normalized by multiplying or dividing by a constant factor, and it can be readily seen that the result is also a solution of the wave equation. For example, if the function ϕ of the coordinates x, y and z satisfies equation (4.18), and the integral of the probability distribution function over the whole of the space in three dimensions is equal to c , then the normalizing factor is $c^{-1/2}$ and the normalized eigenfunction is $c^{-1/2}\phi$. Since $c^{-1/2}$ is a constant quantity and is independent of the coordinates x, y and z , it is evident that $c^{-1/2}\phi$ satisfies the wave equation just as well as does the unnormalized function ϕ .

If ψ_i and ψ_j represent two different eigenfunctions both of which are satisfactory solutions of the wave equation for a given system then, as seen above, these functions will be normalized if

$$\int \psi_i\psi_i^*d\tau = 1 \quad \text{and} \quad \int \psi_j\psi_j^*d\tau = 1. \quad (5.2)$$

Further, if the two eigenfunctions have the property that

$$\int \psi_i \psi_j^* = 0 \quad \text{or} \quad \int \psi_i^* \psi_j = 0, \quad (5.3)$$

they are said to be mutually *orthogonal*.

The normalized, orthogonal functions of the well-behaved class that satisfy the Schrodinger equation have an important property; they can be expanded as a series of other orthogonal functions of the same variables. For example, if ψ is any function that can be expanded in this manner, then

$$\psi = c_1 \phi_1 + c_2 \phi_2 + \cdots + c_i \phi_i + \cdots, \quad (5.4)$$

where the coefficients $c_1, c_2, \cdots, c_i, \cdots$, are constants, and $\phi_1, \phi_2, \cdots, \phi_i, \cdots$, are a set of mutually orthogonal eigenfunctions of the same variables as ψ . If both sides of equation (5.4) are multiplied by ϕ_i^* and then integrated over the whole of the configuration space, the result is

$$\int \phi_i^* \psi d\tau = c_1 \int \phi_i^* \phi_1 d\tau + c_2 \int \phi_i^* \phi_2 d\tau + \cdots + c_i \int \phi_i^* \phi_i d\tau + \cdots \quad (5.5)$$

Since the ϕ functions are mutually orthogonal, all the integrals vanish except the one involving ϕ_i , and this particular integral is equal to unity if the functions are normalized; under these conditions, therefore,

$$\int \phi_i^* \psi d\tau = c_i, \quad (5.6)$$

and hence the values of all the coefficients $c_1, c_2, \cdots, c_i, \cdots$, can be found.

If the eigenfunction ψ is expressed in the form of equation (5.4), the complex conjugate ψ^* can be written as

$$\psi^* = c_1^* \phi_1^* + c_2^* \phi_2^* + \cdots + c_i^* \phi_i^* + \cdots. \quad (5.7)$$

The condition that ψ is normalized is then given by

$$\int \psi \psi^* d\tau = \int (c_1 \phi_1 + c_2 \phi_2 + \cdots)(c_1^* \phi_1^* + c_2^* \phi_2^* + \cdots) d\tau = 1. \quad (5.8)$$

All terms of the type $\int \phi_i \phi_j^* d\tau$ are zero when i and j are different, because of orthogonality, and are equal to unity when i and j are identical, because of normalization. It immediately follows from equation (5.8), therefore, that

$$c_1 c_1^* + c_2 c_2^* + \cdots + c_i c_i^* + \cdots = 1, \quad (5.9)$$

or,

$$\sum_i c_i c_i^* = 1. \quad (5.10)$$

ALTERNATIVE DERIVATION OF WAVE EQUATION

6. Operator Derivation of the Wave Equation.—The derivation of the Schrödinger equation (4.18) was based on certain postulates related to the propagation of waves, but it was stated previously that the same equation may be obtained by the use of postulates that apparently have no relation to wave motion. One particular approach has proved of special importance and this will be considered here. It is based on the concept that to each observable quantity in classical mechanics, e.g., position, momentum or energy, there corresponds a certain mathematical operator, the nature of which is postulated by the new quantum mechanics. The particular postulates which will be made are as follows:

1. The operation corresponding to a coordinate of position (q) is multiplication by the value of that coordinate.

2. The operation representing momentum (p) is the differential operator

$$\frac{h}{2\pi i} \cdot \frac{\partial}{\partial q},$$

where h is the Planck constant and i , as before, is equal to $\sqrt{-1}$.

In addition to these postulates, the usual assumption is made that there is a function ψ of the coordinates which is single valued, continuous, and finite throughout the configuration space, such that $\psi\psi^*$ represents the probability distribution function, as defined in Section 5a, of the system under consideration. If A is the operator equivalent of an observable quantity or property—in the treatment given below this will be the total energy—and a is the precise value of that property in a given state of the system, then it is postulated that operation by A on the function ψ , which is supposed to be suitable for this operator, is equivalent to multiplying ψ by the quantity a ; thus,

$$A\psi = a\psi. \quad (6.1)$$

For the given state, known as the *eigenstate* of the system, ψ is the eigenfunction for the operator A , and a is the corresponding eigenvalue. It may be mentioned here that in certain cases two or more eigenfunctions correspond to the same eigenvalue and belong to the same eigenstate; the state is then said to be *degenerate*.

With these several postulates in mind, it will now be shown that it is possible to derive the Schrödinger equation in a relatively simple manner. Consider a single particle, e.g., an electron, of mass m , moving in a field of force corresponding to a potential $V(x, y, z)$, or V in brief; this potential is a function of the rectangular coordinates x , y and z , and hence the appropriate quantum mechanical operator will be represented by the same expression, i.e., $V(x, y, z)$. The operators for the momenta p_x , p_y and p_z in the directions of the three axes at right angles are

$$p_x = \frac{h}{2\pi i} \cdot \frac{\partial}{\partial x}, \quad p_y = \frac{h}{2\pi i} \cdot \frac{\partial}{\partial y} \quad \text{and} \quad p_z = \frac{h}{2\pi i} \cdot \frac{\partial}{\partial z}, \quad (6.2)$$

and since the total momentum p is related to the three components by the expression

$$p^2 = p_x^2 + p_y^2 + p_z^2, \quad (6.3)$$

it follows that the operator for p^2 may be written as

$$p^2 = -\frac{h^2}{4\pi^2} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right), \quad (6.4)$$

taking into account the rules of operator multiplication. Introducing the abbreviation of equation (4.11) for the Laplacian operator, it follows that

$$p^2 = -\frac{h^2}{4\pi^2} \nabla^2. \quad (6.5)$$

The total energy E of the system is equal to the sum of the kinetic energy T and the potential energy V ; that is,

$$E = T + V. \quad (6.6)$$

The kinetic energy may be represented by $p^2/2m$ [cf. equation (4.15)], and hence

$$E = \frac{p^2}{2m} + V. \quad (6.7)$$

This may be converted into the corresponding operator for energy by utilizing equation (6.5) for the operator for p^2 , and remembering that the operator for the potential energy V is V itself. Hence the quantum mechanical operator for the energy E , generally called the *Hamiltonian operator* and represented by the symbol \mathbf{H} , is given by

$$\mathbf{H} = -\frac{h^2}{8\pi^2m} \nabla^2 + V. \quad (6.8)$$

If E is the precise value (eigenvalue) of the total energy in a given state (eigenstate) of the system, then it follows from equation (6.1) that

$$\mathbf{H}\psi = E\psi, \quad (6.9)$$

or

$$\mathbf{H}\psi - E\psi = 0, \quad (6.10)$$

where ψ is the appropriate eigenfunction which is a function of the coordinates x , y and z . Introducing the expression for the Hamiltonian operator given by equation (6.8), it is seen that

$$\left(-\frac{h^2}{8\pi^2m} \nabla^2 + V \right) \psi - E\psi = 0, \quad (6.11)$$

$$\therefore \nabla^2\psi + \frac{8\pi^2m}{h^2} (E - V)\psi = 0, \quad (6.12)$$

which is identical with the Schrödinger wave equation (4.17). It may be mentioned that the Schrodinger equation is often written in the form of equation (6.9) or (6.10); this is, of course, identical with equation (6.12) with the understanding that the Hamiltonian energy operator is defined by equation (6.8).

APPLICATIONS OF THE WAVE EQUATION: PARTICLE IN A BOX

7. Particle in a Box.—A simple application of the wave equation, the results of which will be employed in Chapter VIII, is to the system generally referred to as a *particle in a box*.

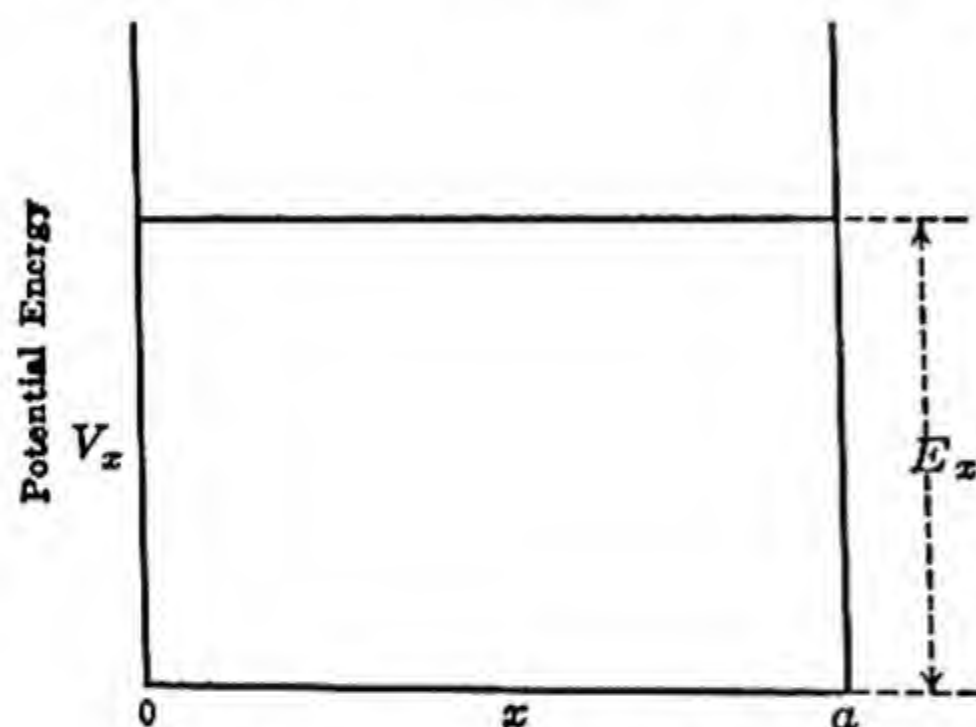


FIG. 2. Energy of particle in a box

A single particle, e.g., a gas molecule, is imagined to be confined between two vertical potential barriers, in each of three directions, x , y and z , at right angles. The potential barriers in the x direction are represented diagrammatically in Fig. 2. The respective distances between the pair of barriers in the three directions are a , b and c ; hence, the situation is equivalent to a particle confined in a rectangular box, with edges of length a , b and c , respectively. Inside the box

the potential function $V(x, y, z)$ is equal to zero, but at the walls it rises suddenly to a very large value.

Let m be the mass of the particle and E its total energy; the wave equation may be written in a slight modification of the usual form, viz.,

$$-\frac{h^2}{8\pi^2m} \left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right) = (E - V)\psi, \quad (7.1)$$

and since V is zero, provided the particle remains within the box, this becomes

$$-\frac{h^2}{8\pi^2m} \left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right) = E\psi. \quad (7.2)$$

As before, the eigenfunction ψ is a function of the coordinates x , y and z .

To solve equation (7.2) it is convenient to separate the three variables, and this can be done by making the assumption that ψ can be written as

$$\psi = X(x)Y(y)Z(z), \quad (7.3)$$

where $X(x)$ is a function of x only, $Y(y)$ of y only, and $Z(z)$ of z only. Substituting this expression for ψ into equation (7.2) and rearranging, it is

found that

$$-\frac{h^2}{8\pi^2m} \left(\frac{1}{X} \cdot \frac{\partial^2 X}{\partial x^2} + \frac{1}{Y} \cdot \frac{\partial^2 Y}{\partial y^2} + \frac{1}{Z} \cdot \frac{\partial^2 Z}{\partial z^2} \right) = E. \quad (7.4)$$

Since $X(x)$ is a function of x alone, the term involving $X(x)$, i.e.,

$$\frac{1}{X} \cdot \frac{\partial^2 X}{\partial x^2}, \quad (7.5)$$

is independent of y and z ; similarly, the corresponding term containing $Y(y)$ does not depend on x and z , and that with $Z(z)$ does not change when x and y are altered. The sum of the three terms, however, after multiplying by the factor $-h^2/8\pi^2m$, is equal to a constant amount, namely the energy E . It follows, therefore, that the term given in (7.5) is independent of x , as well as of y and z , and hence must be constant; similar considerations apply to the analogous terms involving $Y(y)$ and $Z(z)$.

If the total energy is divided into three independent parts, E_x , E_y and E_z , representing the components of the energy in directions parallel to the three coordinates, equation (7.4) may be separated into three equations of the same form in x , y and z , respectively, the one in x being

$$-\frac{h^2}{8\pi^2m} \left(\frac{1}{X} \cdot \frac{\partial^2 X}{\partial x^2} \right) = E_x. \quad (7.6)$$

The general solution of this equation is

$$X(x) = A \sin (Bx + C), \quad (7.7)$$

where A , B and C are constants whose values can be determined from a consideration of the boundary conditions.

In accordance with the usual postulate of quantum mechanics, the probability of finding the particle at any point within the box is related to the square of the absolute value of the function ψ at that point. Hence $|X|^2$, which is a function of the x coordinate only, determines the probability of the particle being found somewhere along the x axis. Since the potential rises to infinity at the walls of the box, the probability of the particle being in the walls will be zero; consequently, $|X|^2$, and hence $X(x)$, must be zero when $x = 0$ and $x = a$, these being the x coordinates of the two potential walls perpendicular to the x axis (Fig. 2). The boundary conditions which satisfy these requirements in equation (7.7) are

$$\sin C = 0 \quad \text{and} \quad \sin (Ba + C) = 0, \quad (7.8)$$

from which it follows that

$$B = \frac{n_x\pi}{a} \quad \text{and} \quad C = 0, \quad (7.9)$$

where n_x is an integer. Inserting these values for B and C in equation (7.7), it is found that

$$X(x) = A \sin \frac{n_x \pi}{a} x, \quad (7.10)$$

and substitution of this result in equation (7.6) gives

$$E_x = \frac{n_x^2 h^2}{8a^2 m}, \quad (7.11)$$

in which the integer n_x may be regarded as a quantum number determining the possible values of the (translational) energy of the particle in the direction parallel to the x axis. Similar equations can be derived for the energies E_y and E_z in the y and z directions, respectively; these are

$$E_y = \frac{n_y^2 h^2}{8b^2 m} \quad \text{and} \quad E_z = \frac{n_z^2 h^2}{8c^2 m}. \quad (7.12)$$

These equations, for various integral values of the quantum numbers n_x , n_y and n_z , give the permitted levels for the translational energy, in directions parallel to the three rectangular axes, of a particle constrained to remain within a box. The total energy E , which is the sum of E_x , E_y and E_z , is then given by

$$E = E_x + E_y + E_z \quad (7.13)$$

$$= \frac{h^2}{8m} \left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right). \quad (7.14)$$

It is of interest to note that since h^2/m is very small for a normal molecule—of the order of 10^{-30} —the separation of successive translational energy levels is so small, for reasonable values of the quantum numbers, that the distribution of energy may be regarded as virtually continuous. It is for this reason that under ordinary conditions the translational motion of a molecule may be adequately treated by the methods of classical mechanics.

THE HARMONIC OSCILLATOR

✓ **8a. Linear Harmonic Oscillator.**—The next case to be considered is that of the linear harmonic oscillator; the results are not only of general interest, but they are also of importance in connection with the study of molecular spectra (Chapter IV). For a particle undergoing simple harmonic oscillations in one dimension, the restoring force is proportional to the displacement x from the equilibrium position; this condition may be expressed mathematically in the form of the equation

$$m \frac{d^2 x}{dt^2} = -kx, \quad (8.1)$$

$$\therefore -\frac{m}{x} \cdot \frac{d^2 x}{dt^2} = k, \quad (8.2)$$

where m is the mass of the oscillating particle and k is a constant. The equation (8.2) is analogous to equation (7.6), and hence the solution is of the same form as (7.7), viz.,

$$x = A \sin (Bt + C), \quad (8.3)$$

where A , B and C are constants. Since the motion is periodic in character, the conditions repeating themselves exactly after each oscillation, it follows that

$$B = 2\pi\nu, \quad (8.4)$$

where ν is the frequency of oscillation of the particle under consideration. Insertion of this value for B in equation (8.3) gives

$$x = A \sin (2\pi\nu t + C), \quad (8.5)$$

and substitution in equation (8.2) then leads to the result

$$k = 4\pi^2\nu^2 m. \quad (8.6)$$

The potential energy V of the oscillator is equal to $\frac{1}{2}kx^2$, and hence

$$V = 2\pi^2\nu^2 mx^2. \quad (8.7)$$

This expression, derived by the methods of classical mechanics, gives the potential function required for the solution of the wave equation in terms of the frequency ν sec.⁻¹ of a classical harmonic oscillator.

For a particle oscillating in one direction only, e.g., parallel to the x axis, the coordinates y and z remain constant; hence, in this case, the wave equation (4.18) reduces to the one-dimensional form

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2m}{h^2} (E - V)\psi = 0, \quad (8.8)$$

in which ψ is an appropriate eigenfunction, and E is the corresponding eigenvalue of the total energy. Inserting the value of the potential energy given by equation (8.7), this becomes

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2m}{h^2} (E - 2\pi^2\nu^2 mx^2)\psi = 0. \quad (8.9)$$

To simplify the form of this differential equation, let

$$a = \frac{8\pi^2mE}{h^2} \quad \text{and} \quad b = \frac{4\pi^2\nu^2 m}{h}; \quad (8.10)$$

then equation (8.9) can be written as

$$\frac{d^2\psi}{dx^2} + (a - bx^2)\psi = 0. \quad (8.11)$$

Introducing, in place of x , a new dimensionless variable q , defined by

$$q = x\sqrt{b}, \quad (8.12)$$

then

$$\frac{d}{dx} = \sqrt{b} \frac{d}{dq} \quad (8.13)$$

and

$$\frac{d^2}{dx^2} = b \frac{d^2}{dq^2}, \quad (8.14)$$

and hence equation (8.11) becomes

$$\frac{d^2\psi}{dq^2} + \left(\frac{a}{b} - q^2\right)\psi = 0. \quad (8.15)$$

The solutions $\psi(x)$ of this equation must, of course, satisfy the condition of a well-behaved function, as described previously; that is to say, the eigenfunctions must be continuous, single valued and finite for all values of x from $-\infty$ to $+\infty$.

8b. Harmonic Oscillator: Asymptotic Solution.—In solving equation (8.15) an attempt is first made to obtain an asymptotic solution for the case in which q is very large, i.e., $q \gg \sqrt{a/b}$; under these conditions the equation becomes

$$\frac{d^2\psi}{dq^2} - q^2\psi = 0, \quad (8.16)$$

solutions of which are

$$\psi = e^{\pm q^2/2}. \quad (8.17)$$

This may be verified by differentiation with respect to q ; thus

$$\frac{d^2\psi}{dq^2} = q^2 e^{\pm q^2/2} \pm e^{\pm q^2/2} \quad (8.18)$$

$$= (q^2 \pm 1) e^{\pm q^2/2}. \quad (8.19)$$

Since q is very large, $q^2 \pm 1$ is not appreciably different from q^2 , and so equation (8.19) becomes

$$\frac{d^2\psi}{dq^2} = q^2 e^{\pm q^2/2} = q^2\psi, \quad (8.20)$$

as required by equation (8.16).

The quantity $|\psi|^2$ is related to the probability of finding the particle somewhere along the x axis; hence, it must decrease continuously to zero as x approaches $-\infty$ on the one hand, and $+\infty$ on the other hand. It is obvious, therefore, that of the two possible solutions given by equation (8.17), viz.,

$$\psi = e^{q^2/2} \quad \text{and} \quad \psi = e^{-q^2/2}, \quad (8.21)$$

the former is not an acceptable wave function, for it increases rapidly with

increasing q , and hence with increasing numerical value of x . The alternative solution, i.e., $\psi = e^{-q^2/2}$, however, satisfies the necessary conditions, and so it may be regarded as a satisfactory asymptotic solution of the wave equation.

8c. Recursion Formula.—Returning now to the original wave equation (8.15), it is probable that the solution will contain the term $e^{-q^2/2}$ as a factor; a possible form of the solution will be

$$\psi = e^{-q^2/2} f(q), \quad (8.22)$$

where $f(q)$ is a function of q , and hence of x , the nature of which is to be determined. On differentiating equation (8.22), it is seen that

$$\frac{d^2\psi}{dq^2} = e^{-q^2/2} \left\{ \frac{d^2f}{dq^2} - 2q \frac{df}{dq} + (q^2 - 1)f \right\}, \quad (8.23)$$

in which f is written for $f(q)$. Substitution for $d^2\psi/dq^2$ and ψ , as given by equations (8.22) and (8.23), into equation (8.15), yields the result

$$e^{-q^2/2} \left\{ \frac{d^2f}{dq^2} - 2q \frac{df}{dq} + (q^2 - 1)f \right\} + e^{-q^2/2} \left(\frac{a}{b} - q^2 \right) f = 0, \quad (8.24)$$

$$\therefore e^{-q^2/2} \left\{ \frac{d^2f}{dq^2} - 2q \frac{df}{dq} + \left(\frac{a}{b} - 1 \right) f \right\} = 0. \quad (8.25)$$

Since $e^{-q^2/2}$ is not zero, except for $q = \pm \infty$, it follows that the expression in the brackets must be zero; that is,

$$\frac{d^2f}{dq^2} - 2q \frac{df}{dq} + \left(\frac{a}{b} - 1 \right) f = 0. \quad (8.26)$$

The assumption is now made that $f(q)$ may be expressed in the form of a power series in q ; thus,

$$f(q) = \alpha_0 + \alpha_1 q + \alpha_2 q^2 + \alpha_3 q^3 + \alpha_4 q^4 + \dots; \quad (8.27)$$

then

$$\frac{df}{dq} = \alpha_1 + 2\alpha_2 q + 3\alpha_3 q^2 + 4\alpha_4 q^3 + 5\alpha_5 q^4 + \dots, \quad (8.28)$$

and

$$\frac{d^2f}{dq^2} = 2\alpha_2 + 6\alpha_3 q + 12\alpha_4 q^2 + 20\alpha_5 q^3 + 30\alpha_6 q^4 + \dots. \quad (8.29)$$

Insertion of these expressions in equation (8.26) then gives

$$\begin{aligned} & 2\alpha_2 + 6\alpha_3 q + 12\alpha_4 q^2 + 20\alpha_5 q^3 + \dots \\ & - 2\alpha_1 q - 4\alpha_2 q^2 - 6\alpha_3 q^3 - \dots \\ & + \left(\frac{a}{b} - 1 \right) \alpha_0 + \left(\frac{a}{b} - 1 \right) \alpha_1 q + \left(\frac{a}{b} - 1 \right) \alpha_2 q^2 + \left(\frac{a}{b} - 1 \right) \alpha_3 q^3 + \dots = 0, \end{aligned} \quad (8.30)$$

the values for the three terms being arranged vertically in increasing powers of q . In order for this series to vanish for all values of q , as is necessary if $f(q)$ is to be a solution of equation (8.26), the coefficients of individual powers of q must vanish separately. Hence, for the coefficient of q^0 ,

$$2\alpha_2 + \left(\frac{a}{b} - 1\right)\alpha_0 = 0; \quad \checkmark \quad (8.31)$$

for the coefficient of q^1 ,

$$6\alpha_3 - 2\alpha_1 + \left(\frac{a}{b} - 1\right)\alpha_1 = 0; \quad (8.32)$$

for the coefficient of q^2 ,

$$12\alpha_4 - 4\alpha_2 + \left(\frac{a}{b} - 1\right)\alpha_2 = 0. \quad (8.33)$$

In general, for the coefficient of q^n to vanish,

$$(n+1)(n+2)\alpha_{n+2} - 2n\alpha_n + \left(\frac{a}{b} - 1\right)\alpha_n = 0, \quad (8.34)$$

and, consequently,

$$\frac{\alpha_{n+2}}{\alpha_n} = \frac{2n - \frac{a}{b} + 1}{(n+1)(n+2)}, \quad (8.35)$$

where n is an integer or zero. This *recursion formula*, as it is called, permits the calculation of the coefficient α_{n+2} of the term involving q^{n+2} in the power series for $f(q)$, i.e., equation (8.27), provided the coefficient α_n of q^n is known. Thus, from the coefficient of q^0 , it is possible to derive that of q^2 , and hence of q^4 , q^6 , etc.; similarly, if the coefficient of q^1 is known, those of q^3 , q^5 , etc., can be calculated.

8d. Energy Levels of Harmonic Oscillator.—If no restriction is placed on the value of the fraction a/b , which is related to the energy E of the oscillator by the equations (8.10), the function ψ , as defined by $e^{-q^2/2}f(q)$, may prove to be unacceptable, for it may increase rapidly with increasing q , and consequently with increasing x . This may be seen in the following manner. Consider the series for e^{q^2} , viz.,

$$e^{q^2} = 1 + q^2 + \frac{q^4}{2!} + \cdots + \frac{q^n}{(\frac{1}{2}n)!} + \cdots \quad (8.36)$$

The coefficient of q^n , which may be represented by β_n , is $1/(\frac{1}{2}n)!$, while that of q^{n+2} , represented by β_{n+2} , is $1/(\frac{1}{2}n+1)!$. The recursion formula for the exponential series for e^{q^2} is thus given by

$$\frac{\beta_{n+2}}{\beta_n} = \frac{(\frac{1}{2}n)!}{(\frac{1}{2}n+1)!} = \frac{1}{\frac{1}{2}n+1}. \quad (8.37)$$

In the limit, when n is very large, so that unity is negligible in comparison with $\frac{1}{2}n$, this becomes

$$\lim_{n \rightarrow \infty} \frac{\beta_{n+2}}{\beta_n} = \frac{2}{n}. \quad (8.38)$$

Examination of equation (8.35) shows that when n is very large, the recursion formula for the power series representing $f(q)$ also becomes

$$\lim_{n \rightarrow \infty} \frac{\alpha_{n+2}}{\alpha_n} = \frac{2}{n}, \quad (8.39)$$

so that for large values of the exponent n the series for $f(q)$ will behave like that for e^{q^2} . If this is the case, then according to equation (8.22) the eigenfunction ψ for large values of n will become equivalent to $e^{-q^2/2} \times e^{q^2}$, and hence to $e^{q^2/2}$. It has been already seen that a function of this kind cannot be an acceptable wave function, since this quantity increases as q increases. The series governed by the recursion formula of equation (8.29) cannot therefore form part of a satisfactory eigenfunction unless some restriction is introduced which makes the series break off after a finite number of terms. In other words, the expression for $f(q)$, as given by equation (8.27), should be restricted in such a manner as to make it a polynomial rather than a power series. The eigenfunction ψ can then be set equal to the product of this polynomial and the factor $e^{-q^2/2}$. Since the value of the latter decreases with increasing q , and hence with increasing x , the eigenfunction as a whole will behave in the same manner. Such a function will evidently satisfy the conditions for a suitable wave function.

By setting the numerator in the recursion formula (8.35) equal to zero, that is, if

$$\frac{a}{b} - 1 - 2n = 0, \quad (8.40)$$

or

$$\frac{a}{b} = 2n + 1, \quad (8.41)$$

the series for $f(q)$ will break off after the term q^n , since the coefficient of q^{n+2} , and of all higher terms, will be zero. This is the condition, therefore, that makes the series $f(q)$ a polynomial, so that $e^{-q^2/2}f(q)$ will be a satisfactory wave function. Substituting the values of a and b given by the equations (8.10) into equation (8.41), it is seen that the restriction that makes the wave function suitable is

$$\frac{2E}{h\nu} = 2n + 1, \quad (8.42)$$

or

$$E_n = (n + \frac{1}{2})h\nu, \quad (8.43)$$

where n , as previously indicated, is zero or integral. This result implies that the Schrödinger equation for a linear harmonic oscillator can have physically

acceptable solutions only for certain discrete values of the energy. These values, represented by E_n and given by equation (8.43), for $n = 0, 1, 2, \dots$, are the appropriate eigenvalues.

8e. Eigenfunctions of Harmonic Oscillator.—The corresponding eigenfunctions ψ_n can be derived from equation (8.9) as functions of x . Without going into details, since the results will be employed only indirectly in this book, it may be stated that the eigenfunctions are of the form

$$\psi_n = N_n e^{-q^2/2} H_n(q), \quad (8.44)$$

where q has the same significance as before [equation (8.12)], N_n is a normalizing factor, and $H_n(q)$ represents a *Hermite polynomial* of degree n , defined by

$$H_n(q) = (-1)^n e^{q^2} \frac{d^n e^{-q^2}}{dq^n}. \quad (8.45)$$

The first few Hermite polynomials, for $n = 0, 1, 2$ and 3 , are as follows:

$$\begin{aligned} n = 0, & \quad H_0(q) = 1 \\ n = 1, & \quad H_1(q) = 2q \\ n = 2, & \quad H_2(q) = 4q^2 - 2 \\ n = 3, & \quad H_3(q) = 8q^3 - 12q. \end{aligned} \quad (8.46)$$

These can be converted into functions of the displacement x of the harmonic oscillator by making use of equations (8.10) and (8.12).

8f. Zero-Point Energy.—An important consequence of equation (8.43) is the existence of the so-called *zero-point energy*, or *residual energy*. The lowest possible energy E_0 of an oscillator occurs when n is zero; thus

$$E_0 = \frac{1}{2} h \nu, \quad (8.47)$$

where ν is the frequency of the oscillator in sec^{-1} . This is sometimes written as $E_0 = \frac{1}{2} h c \nu$, where ν is now the frequency in wave numbers, i.e., in cm^{-1} units, and c is the velocity of light. It is seen from equation (8.47) that even in the vicinity of the absolute zero of temperature, when the vibrational energy of a molecular oscillator has its lowest possible value, that value would still not be less than the zero-point energy of $\frac{1}{2} h \nu$ per oscillator whose frequency is $\nu \text{ sec}^{-1}$. The existence of this zero-point energy is, in fact, an aspect of the uncertainty principle. It might be imagined that at the absolute zero, at least, the internal motions of a molecule would cease entirely, so that the positions of the constituent atoms could be identified exactly. This is not the case, however; since the molecule still has vibrational energy, equal to $\frac{1}{2} h \nu$ for each oscillator, the atoms are in a state of vibration even at the absolute zero, and so their precise position cannot be defined.

It is of interest to note here that the older quantum theory led to the equation $E_n = n h \nu$ for the energy levels of a linear oscillator. It was evident

from a study of the vibrational spectra of molecules, however, that an expression of this kind did not define correctly the energy of a harmonic oscillator of two atoms vibrating relative to each other (see Chapter IV). By utilizing equation (8.43), derived from quantum mechanics, the conclusions reached are in satisfactory agreement with the results of spectroscopic studies.

THE RIGID ROTATOR

9a. Rigid Rotator with Free Axis.—Consider two spherical particles, of masses m_1 and m_2 , situated at fixed distances r_1 and r_2 , respectively, from the center of gravity of the system (Fig. 3). The distance between the mass centers of the particles then has the constant value r_0 , which is equal to the sum of r_1 and r_2 . It is supposed that this system rotates about an axis passing through the center of gravity, and normal to a plane containing the two particles. Such a system constitutes a *rigid rotator*, the term rigid being employed because of the fixed distance between the particles. If these particles are constrained to remain in one plane, then the direction of the axis of rotation is fixed, and the system is described as a rigid rotator with *fixed axis*. The case of particular interest, especially in connection with the study of molecular spectra and the rotational energies of molecules (Chapters IV and VIII), is that in which the plane of the particles can move, and so the axis of rotation is free to take up any position. The rigid rotator with *free axis* as thus described is somewhat analogous to a diatomic molecule. In the latter case, however, the atoms vibrate with respect to each other, and so the system is not really rigid. Since the distance apart of the equilibrium positions is constant, however, the diatomic molecule may be treated, at least as a first approximation, as a rigid rotator with free axis.

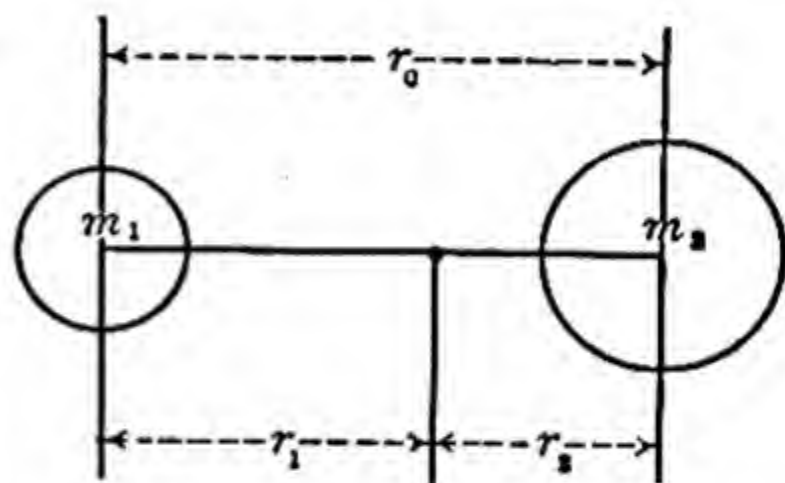


FIG. 3. Rigid rotator

9b. Energy and Moment of Inertia of Rotator.—The kinetic energy T of a particle, equal to $\frac{1}{2}mv^2$, may also be expressed as

$$T = \frac{1}{2}mv^2 = \frac{1}{2}m(\dot{x}^2 + \dot{y}^2 + \dot{z}^2), \quad (9.1)$$

where \dot{x} , \dot{y} and \dot{z} represent the components of the velocity v parallel to three axes at right angles.⁴ In order to express this result in terms of spherical coordinates (Fig. 4), the usual transformations are made, namely

$$x = r \sin \theta \cos \phi, \quad (9.2)$$

$$y = r \sin \theta \sin \phi, \quad (9.3)$$

$$z = r \cos \theta, \quad (9.4)$$

⁴ In accordance with the usual convention, a dot placed over a letter implies a derivative with respect to time; thus, $\dot{x} = \partial x / \partial t$.

and it is then found that

$$T = \frac{1}{2}m(\dot{r}^2 + r^2\dot{\theta}^2 + r^2\dot{\phi}^2 \sin^2 \theta). \quad (9.5)$$

If the distance r of the particle from the origin is fixed, the derivatives \dot{r} and \ddot{r} are zero; hence the equation for the kinetic energy becomes

$$T = \frac{1}{2}mr^2(\dot{\theta}^2 + \dot{\phi}^2 \sin^2 \theta). \quad (9.6)$$

For the two particles forming a rigid rotator the total kinetic energy is given by the sum of two expressions similar to that in equation (9.6), since in each case the term involving \dot{r}^2 is zero. It follows, therefore, for the rotator under consideration that

$$T = \frac{1}{2}m_1r_1^2(\dot{\theta}^2 + \dot{\phi}^2 \sin^2 \theta) + \frac{1}{2}m_2r_2^2(\dot{\theta}^2 + \dot{\phi}^2 \sin^2 \theta). \quad (9.7)$$

It should be noted that the rigid rotator has no potential

energy, and so equation (9.7) gives the total energy E , as well as the kinetic energy. Writing this result in a slightly different form, it follows that

$$E = \frac{1}{2}(m_1r_1^2 + m_2r_2^2)(\dot{\theta}^2 + \dot{\phi}^2 \sin^2 \theta). \quad (9.8)$$

The expression in the first parentheses is that for the moment of inertia I of the system of two particles; hence equation (9.8) may be written as

$$E = \frac{1}{2}I(\dot{\theta}^2 + \dot{\phi}^2 \sin^2 \theta). \quad (9.9)$$

Comparison of this result with equation (9.6) shows that the rigid rotator behaves like a single particle of mass I placed at a fixed distance, equal to unity (since $r = 1$), from the origin, which in this case is the center of gravity of the system. The rotator is thus equivalent to a particle of mass I moving on the surface of a sphere of radius unity.

The moment of inertia may be expressed in a more convenient form in the following manner. Since the system is rotating about its center of gravity,

$$m_1r_1 = m_2r_2. \quad (9.10)$$

Further, since $r_1 + r_2$ is equal to r_0 , it follows that

$$r_2 = r_0 - r_1, \quad (9.11)$$

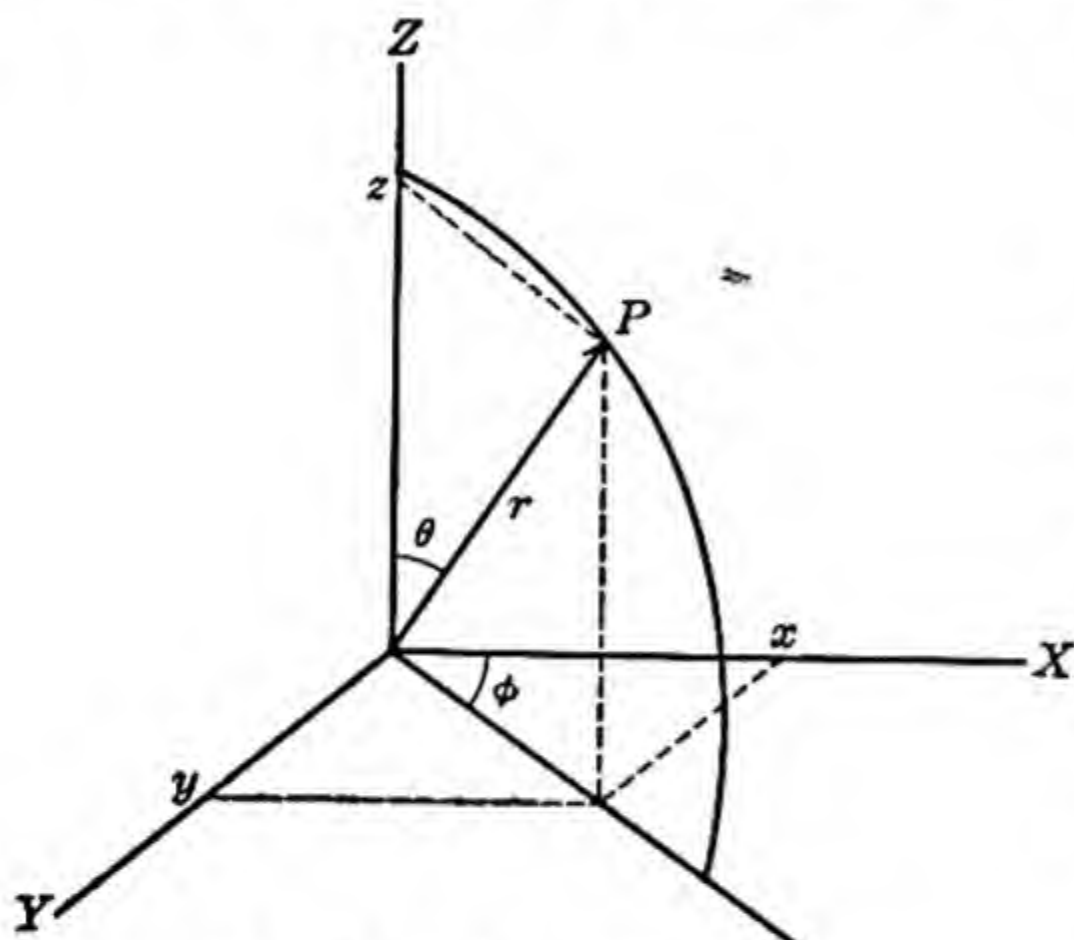


FIG. 4. Spherical coordinates

and consequently from equations (9.10) and (9.11),

$$m_1 r_1 = m_2 r_2 = m_2 (r_0 - r_1), \quad (9.12)$$

$$\therefore r_1 = \frac{m_2}{m_1 + m_2} r_0. \quad (9.13)$$

It is also seen from the same equations that

$$m_1 r_1^2 + m_2 r_2^2 = m_1 r_1 r_0, \quad (9.14)$$

and introduction of equation (9.13) then gives

$$m_1 r_1^2 + m_2 r_2^2 = \frac{m_1 m_2}{m_1 + m_2} r_0^2 \quad (9.15)$$

$$= \mu r_0^2, \quad (9.16)$$

where μ , known as the *reduced mass* of the system, is defined by

$$\mu = \frac{m_1 m_2}{m_1 + m_2}. \quad (9.17)$$

The left-hand side of equation (9.16) is equal to the moment of inertia I , and hence the latter may be conveniently represented by the equation

$$I = \mu r_0^2. \quad (9.18)$$

9c. Wave Equation for Rotator.—The Schrödinger equation (4.18), in three dimensions, is

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0, \quad (9.19)$$

and if this is converted into spherical coordinates, the result is

$$\frac{1}{r^2} \cdot \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \cdot \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \cdot \frac{\partial^2 \psi}{\partial \phi^2} + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0. \quad (9.20)$$

For the rigid rotator, as seen above, the mass m may be replaced by the moment of inertia I , and r by unity; further, the potential energy V is zero, and so the wave equation reduces to

$$\frac{1}{\sin \theta} \cdot \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \cdot \frac{\partial^2 \psi}{\partial \phi^2} + \frac{8\pi^2 I E}{h^2} \psi = 0. \quad (9.21)$$

This is a differential equation with two independent variables, ϕ and θ , representing the rotation of the system and the precessional motion of its

(free) axis, respectively. In order to solve equation (9.21) an attempt is made to separate the variables; that is to say, it is supposed that the function, represented briefly by $\psi(\theta, \phi)$, can be regarded as equivalent to the product of two functions, namely, $Y(\theta)$ and $Z(\phi)$, each involving one variable only, i.e.,

$$\psi(\theta, \phi) = Y(\theta)Z(\phi). \quad (9.22)$$

By successive differentiation of this expression it is found that

$$\frac{\partial \psi}{\partial \theta} = Z(\phi) \frac{dY}{d\theta} \quad \text{and} \quad \frac{\partial \psi}{\partial \phi} = Y(\theta) \frac{dZ}{d\phi}, \quad (9.23)$$

and

$$\frac{\partial^2 \psi}{\partial \theta^2} = Z(\phi) \frac{d^2 Y}{d\theta^2} \quad \text{and} \quad \frac{\partial^2 \psi}{\partial \phi^2} = Y(\theta) \frac{d^2 Z}{d\phi^2}. \quad (9.24)$$

Substitution of these results in equation (9.21) then yields

$$\frac{Z}{\sin \theta} \cdot \frac{d}{d\theta} \left(\sin \theta \frac{dY}{d\theta} \right) + \frac{Y}{\sin^2 \theta} \cdot \frac{d^2 Z}{d\phi^2} + \beta YZ = 0, \quad (9.25)$$

where β is defined by

$$\beta = \frac{8\pi^2 IE}{h^2}. \quad (9.26)$$

Multiplying through equation (9.25) by the quantity $\sin^2 \theta / YZ$, which never becomes infinite, it is seen that

$$\frac{\sin \theta}{Y} \cdot \frac{d}{d\theta} \left(\sin \theta \frac{dY}{d\theta} \right) + \beta \sin^2 \theta = -\frac{1}{Z} \cdot \frac{d^2 Z}{d\phi^2}, \quad (9.27)$$

in which the left-hand side involves the variable θ only, while the right-hand side depends on ϕ only, the two variables being independent. This relationship must be valid for any possible values of θ and ϕ , so it is apparent that each side of equation (9.27) must be constant. That this is the case may be readily shown by the following argument. Suppose ϕ is maintained constant while θ is varied; since the right-hand side of equation (9.27) is unchanged, the left-hand side must also be constant, in spite of the variation in θ . Similarly, if θ is kept constant, so that the left-hand side does not vary, the right-hand side must remain the same for all values of ϕ . Both sides of equation (9.27) are thus equal to the same constant, which is represented by the quantity m^2 for convenience;⁶ hence it is possible to write

$$\frac{\sin \theta}{Y} \cdot \frac{d}{d\theta} \left(\sin \theta \frac{dY}{d\theta} \right) + \beta \sin^2 \theta = m^2, \quad (9.28)$$

⁶ It has unfortunately become the custom to use the letter m in this connection, although it has no relationship to mass: as will be seen shortly, m is actually a quantum number.

and

$$-\frac{1}{Z} \cdot \frac{d^2 Z}{d\phi^2} = m^2, \quad (9.29)$$

each equation involving one variable only.

9d. Complex and Real Solutions.—The second of the equations given above may be written in the form

$$\frac{d^2 Z}{d\phi^2} + m^2 Z = 0, \quad (9.30)$$

and the solutions of this are

$$Z = Ce^{im\phi} \quad \text{and} \quad Z = Ce^{-im\phi}, \quad (9.31)$$

where C is an arbitrary constant. The correctness of these solutions can be readily proved by differentiation. In order that the function Z may be single valued, it must of necessity have the same value for $\phi = 0$ and for $\phi = 2\pi$. When ϕ is zero, both solutions, as given by the equations (9.31), take the form

$$Z = C, \quad (9.32)$$

while for ϕ equal to 2π ,

$$Z = Ce^{\pm 2\pi m i}. \quad (9.33)$$

Since the two solutions, equations (9.32) and (9.33), must be identical, it follows that

$$e^{\pm 2\pi m i} = 1. \quad (9.34)$$

The quantity $e^{\pm 2\pi m i}$ can be expressed in terms of trigonometric functions; consequently,

$$e^{\pm 2\pi m i} = \cos 2\pi m \pm i \sin 2\pi m = 1, \quad (9.35)$$

which can be true only if m is zero or an integer.

The constant C in equation (9.31) is arbitrary, and so it may be chosen in such a way that the function Z is normalized, i.e., in order that

$$\int_0^{2\pi} ZZ^* d\phi = 1. \quad (9.36)$$

Inserting the values of Z and Z^* given by equation (9.31), it follows that

$$\begin{aligned} \int_0^{2\pi} ZZ^* d\phi &= C^2 \int_0^{2\pi} e^{\pm im\phi} e^{\mp im\phi} d\phi \\ &= C^2 \int_0^{2\pi} d\phi \\ &= 2\pi C^2. \end{aligned} \quad (9.37)$$

Equating this result to unity, it is found that

$$C = \frac{1}{\sqrt{2\pi}}, \quad (9.38)$$

and hence the normalized functions are

$$Z = \frac{1}{\sqrt{2\pi}} e^{im\phi}, \quad (9.39)$$

where

$$m = 0, \pm 1, \pm 2, \pm 3, \text{ etc.} \quad (9.40)$$

Since the foregoing solutions of equation (9.30) involve the quantity i , they are complex quantities. For certain purposes, however, it is desirable to have alternative solutions which are real; such solutions are

$$Z = C' \sin m\phi \quad \text{and} \quad Z = C' \cos m\phi, \quad (9.41)$$

where C' is a normalization constant different from the one given by equation (9.38). The accuracy of these solutions of equation (9.30) can be proved by differentiation, but it is of interest to indicate how they have been obtained. Since $Ce^{im\phi}$ and $Ce^{-im\phi}$ are solutions of equation (9.30), linear combinations will also be solutions of this equation. By definition

$$2i \sin x = e^{ix} - e^{-ix},$$

and

$$2 \cos x = e^{ix} + e^{-ix},$$

and hence it is apparent that $C' \sin m\phi$ and $C' \cos m\phi$ are linear combinations of $Ce^{im\phi}$ and $Ce^{-im\phi}$, and hence are also solutions of equation (9.30). The value of the normalization constant C' may be determined by the method used above for C ; it is found to be $1/\sqrt{\pi}$, so that

$$Z = \frac{1}{\sqrt{\pi}} \sin m\phi \quad \text{and} \quad Z = \frac{1}{\sqrt{\pi}} \cos m\phi. \quad (9.42)$$

As shown above, the values of m in these solutions must be zero or integral.

9e. Legendre's Equation.—Having found satisfactory solutions of equation (9.30), and hence of (9.29), attention must now be turned to equation (9.28); after multiplying through by $Y/\sin^2 \theta$, this becomes

$$\frac{1}{\sin \theta} \cdot \frac{d}{d\theta} \left(\sin \theta \frac{dY}{d\theta} \right) + \left(\beta - \frac{m^2}{\sin^2 \theta} \right) Y = 0. \quad (9.43)$$

A new variable x is now defined by

$$x = \cos \theta, \quad (9.44)$$

so that

$$\sin \theta = \sqrt{1 - x^2}. \quad (9.45)$$

Consequently,

$$\frac{dY}{d\theta} = \frac{dx}{d\theta} \cdot \frac{dY}{dx} = -\sin \theta \frac{dY}{dx}, \quad (9.46)$$

and hence, in general,

$$\frac{d}{d\theta} = -\sin \theta \frac{d}{dx}. \quad (9.47)$$

Further,

$$\sin \theta \frac{dY}{d\theta} = -\sin^2 \theta \frac{dY}{dx} \quad (9.48)$$

$$= -(1 - x^2) \frac{dY}{dx}. \quad (9.49)$$

Making use of the relationships in equations (9.47) and (9.49) to change the variable from θ to x , equation (9.43) becomes

$$\frac{d}{dx} \left\{ (1 - x^2) \frac{dY}{dx} \right\} + \left(\beta - \frac{m^2}{1 - x^2} \right) Y = 0. \quad (9.50)$$

This equation is of a form familiar to mathematicians, and is known as *Legendre's equation*; in the present case, since x is equal to $\cos \theta$, it can have physical significance only for values of x between the limits of -1 and $+1$. ✓

In order to solve equation (9.50) conveniently by the polynomial method, somewhat similar to that used in connection with the problem of the harmonic oscillator, the function Y should be replaced by another function of x , namely $G(x)$, defined by

$$Y = (1 - x^2)^{1/2} G. \quad (9.51)$$

From this it is readily seen that

$$\frac{dY}{dx} = -mx(1 - x^2)^{1/2} G + (1 - x^2)^{1/2} \frac{dG}{dx}, \quad (9.52)$$

$$\therefore (1 - x^2) \frac{dY}{dx} = -mx(1 - x^2)^{3/2} G + (1 - x^2)^{3/2} \frac{dG}{dx}. \quad (9.53)$$

Hence,

$$\begin{aligned} \frac{d}{dx} \left\{ (1 - x^2) \frac{dY}{dx} \right\} &= \{ -m(1 - x^2)^{3/2} + m^2 x^2 (1 - x^2)^{1/2} \} G \\ &\quad - \{ 2x(m + 1)(1 - x^2)^{3/2} \} G' + (1 - x^2)^{3/2} G'', \end{aligned} \quad (9.54)$$

where

$$G' = \frac{dG}{dx} \quad \text{and} \quad G'' = \frac{d^2 G}{dx^2}. \quad (9.55)$$

Substituting this result for the first term on the left-hand side of equation (9.50) and dividing through by $(1 - x^2)^{1/2}$, which is not zero except at the limits noted above, i.e., when x is $+1$ or -1 , there is obtained the equation

$$(1 - x^2)G'' - 2(m + 1)xG' + \{\beta - m(m + 1)\}G = 0, \quad (9.56)$$

or

$$(1 - x^2)G'' - 2axG' + bG = 0, \quad (9.57)$$

where the abbreviations

$$a = m + 1 \quad \text{and} \quad b = \beta - m(m + 1) \quad (9.58)$$

have been used for simplicity.

As before, the assumption is now made that $G(x)$ can be expressed as a power series; thus,

$$G = \alpha_0 + \alpha_1 x + \alpha_2 x^2 + \alpha_3 x^3 + \dots \quad (9.59)$$

so that,

$$G' = \alpha_1 + 2\alpha_2 x + 3\alpha_3 x^2 + 4\alpha_4 x^3 + \dots \quad (9.60)$$

and

$$G'' = 2\alpha_2 + 6\alpha_3 x + 12\alpha_4 x^2 + 20\alpha_5 x^3 + \dots \quad (9.61)$$

Introducing these expressions into equation (9.57) and arranging the terms vertically according to increasing powers of x , the result is

$$\begin{aligned} & 2\alpha_2 + 6\alpha_3 x + 12\alpha_4 x^2 + 20\alpha_5 x^3 + \dots \\ & \quad - 2\alpha_2 x^2 - 6\alpha_3 x^3 - \dots \\ & \quad - 2a\alpha_1 x - 4a\alpha_2 x^2 - 6a\alpha_3 x^3 - \dots \\ & + b\alpha_0 + b\alpha_1 x + b\alpha_2 x^2 + b\alpha_3 x^3 + \dots = 0. \end{aligned} \quad (9.62)$$

In order that this series may be zero for all possible values of x , the coefficients of individual powers of x must vanish separately; therefore,

$$\begin{aligned} 2\alpha_2 + b\alpha_0 &= 0, \\ 6\alpha_3 + (b - 2a)\alpha_1 &= 0, \\ 12\alpha_4 + (b - 4a - 2)\alpha_2 &= 0, \\ 20\alpha_5 + (b - 6a - 6)\alpha_3 &= 0, \end{aligned}$$

or, in general,

$$(n + 1)(n + 2)\alpha_{n+2} + \{b - 2na - n(n - 1)\}\alpha_n = 0, \quad (9.63)$$

where n is zero or an integer. Inserting the values for a and b , from the equations (9.58), there is obtained the recursion formula

$$\frac{\alpha_{n+2}}{\alpha_n} = \frac{(n + m)(n + m + 1) - \beta}{(n + 1)(n + 2)}, \quad (9.64)$$

for the coefficients in the power series for $G(x)$.

9f. Energy Levels of Rotator.—In order that $G(x)$ may form part of an acceptable wave function ψ , it is necessary that it should be a polynomial, breaking off after a finite number of terms. The condition for this can be found, as before, by equating the numerator of the recursion formula to zero, i.e.,

$$(n + m)(n + m + 1) - \beta = 0, \\ \therefore \beta = (n + m)(n + m + 1). \quad (9.65)$$

It has been already seen that m must be zero or an integer, and since the same condition applies to n , the sum $n + m$, which may be replaced by l , is also zero or integral. It follows, therefore, that the condition for a satisfactory wave function may be written as

$$\beta = l(l + 1), \quad (9.66)$$

where l , equal to $m + n$, may be 0, 1, 2, 3, etc. Introducing the value of β , defined by equation (9.26), it is evident that

$$\frac{8\pi^2 I E}{h^2} = l(l + 1), \quad (9.67)$$

or

$$E_l = l(l + 1) \frac{h^2}{8\pi^2 I}, \quad (9.68)$$

which gives the permitted values (eigenvalues) for the energy of a rigid rotator with free axis.

10a. Legendre Polynomials.—The eigenfunctions corresponding to the eigenvalues given by equation (9.68) are of importance in connection with the hydrogen atom problem to be considered shortly, and so the method of deriving these wave functions will be described in some detail. For this objective it is necessary to possess some knowledge of *Legendre polynomials* and *associated Legendre functions*. There are several ways of approaching this subject, of which the following is perhaps one of the most convenient for the present purpose. Consider the differential equation

$$(1 - x^2) \frac{dy}{dx} + 2lx = 0, \quad (10.1)$$

where l is a constant; this will later be identified with l in the previous section. On separating the variables, equation (10.1) can be put in the form

$$\frac{dy}{y} + \frac{2lx}{1 - x^2} dx = 0, \quad (10.2)$$

and integration gives

$$\ln y - l \ln (1 - x^2) = \text{constant}, \quad (10.3)$$

or

$$\frac{y}{(1-x^2)^l} = \text{constant.} \quad (10.4)$$

The solution of equation (10.1) is thus of the form

$$y = c(1-x^2)^l, \quad (10.5)$$

where c is a constant. The l th derivative of y can then be written as

$$\frac{d^l y}{dx^l} = c \frac{d^l (1-x^2)^l}{dx^l}. \quad (10.6)$$

If equation (10.1) is differentiated n times, the result is

$$(1-x^2) \frac{d^{n+1} y}{dx^{n+1}} + 2(l-n)x \frac{d^n y}{dx^n} + n(2l-n+1) \frac{d^{n-1} y}{dx^{n-1}} = 0. \quad (10.7)$$

In the special case in which n is equal to $l+1$, this equation becomes

$$(1-x^2) \frac{d^{l+2} y}{dx^{l+2}} - 2x \frac{d^{l+1} y}{dx^{l+1}} + l(l+1) \frac{d^l y}{dx^l} = 0, \quad (10.8)$$

or, writing for brevity,

$$z = \frac{d^l y}{dx^l}, \quad (10.9)$$

it follows that

$$(1-x^2) \frac{d^2 z}{dx^2} - 2x \frac{dz}{dx} + l(l+1)z = 0. \quad (10.10)$$

Further, since

$$\frac{d}{dx} \left\{ (1-x^2) \frac{dz}{dx} \right\} = (1-x^2) \frac{d^2 z}{dx^2} - 2x \frac{dz}{dx}, \quad (10.11)$$

it follows that equation (10.10) may be written as

$$\frac{d}{dx} \left\{ (1-x^2) \frac{dz}{dx} \right\} + l(l+1)z = 0. \quad (10.12)$$

This is similar to equation (9.50) and is also a form of the Legendre equation. Making use of the value of $d^l y/dx^l$ given by equation (10.6), it follows that the solution of equation (10.12) is

$$z = c \frac{d^l (1-x^2)^l}{dx^l}. \quad (10.13)$$

In the special case for which the value of the arbitrary constant c is given by

$$c = \frac{(-1)^l}{2^l l!}, \quad (10.14)$$

the resulting solution is the *Legendre polynomial* of degree l , and is represented by the symbol $P_l(x)$; thus

$$P_l(x) = \frac{1}{2^l l!} \cdot \frac{d^l (x^2 - 1)^l}{dx^l}, \quad (10.15)$$

in which the constant term $(-1)^l$ has been combined with $(1 - x^2)^l$ to give $(x^2 - 1)^l$. Incidentally, since the Legendre polynomial is a solution of the Legendre equation (10.12), the latter may be written in the form

$$\frac{d}{dx} \left\{ (1 - x^2) \frac{dP_l(x)}{dx} \right\} + l(l+1)P_l(x) = 0. \quad (10.16)$$

It is a relatively simple matter to evaluate the Legendre polynomials, by means of equation (10.15), for a number of values of l ; some of these are given below. It will be observed that in each polynomial the powers of x are either all even or all odd.

$$\begin{aligned} l = 0, & \quad P_0(x) = 1 \\ l = 1, & \quad P_1(x) = x \\ l = 2, & \quad P_2(x) = \frac{1}{2}(3x^2 - 1) \\ l = 3, & \quad P_3(x) = \frac{1}{2}(5x^3 - 3x) \\ l = 4, & \quad P_4(x) = \frac{1}{8}(35x^4 - 30x^2 + 3). \end{aligned} \quad (10.17)$$

Attention may be called to the fact that it can be shown, although the proof will not be given here, that the Legendre polynomials form an orthogonal system in the interval $-1 \leq x \leq 1$; that is

$$\int_{-1}^1 P_l(x) P_n(x) dx = 0, \quad \text{for } l \neq n. \quad (10.18)$$

The interval referred to is, of course, that which is physically significant for the present problem (see p. 41). The polynomials can be normalized by making use of the result

$$\int_{-1}^1 P_l(x) P_n(x) dx = \frac{2}{2l+1} \quad \text{for } l = n, \quad (10.19)$$

and so the normalizing factor is $\sqrt{(2l+1)/2}$.

10b. Associated Legendre Functions.—Upon differentiating equation (10.16) successively m times, the result is

$$\begin{aligned} (1 - x^2) \frac{d^{m+2} P_l(x)}{dx^{m+2}} - 2(m+1)x \frac{d^{m+1} P_l(x)}{dx^{m+1}} \\ + \{l(l+1) - m(m+1)\} \frac{d^m P_l(x)}{dx^m} = 0. \end{aligned} \quad (10.20)$$

Since the solution of equation (10.16) is the Legendre polynomial $P_l(x)$, it is evident that the solution of equation (10.20) is $d^m P_l(x)/dx^m$. If now a quantity, represented by the symbol $P_l^m(x)$, known as the *associated Legendre function* of degree l and order m , is defined by

$$P_l^m(x) = (1 - x^2)^{1/2m} \frac{d^m P_l(x)}{dx^m}, \quad (10.21)$$

the equation (10.20) can be transformed into

$$(1 - x^2) \frac{d^2 P_l^m(x)}{dx^2} - 2x \frac{dP_l^m(x)}{dx} + \left\{ l(l+1) - \frac{m^2}{1-x^2} \right\} P_l^m(x) = 0, \quad (10.22)$$

or

$$\frac{d}{dx} \left\{ (1 - x^2) \frac{dP_l^m(x)}{dx} \right\} + \left\{ l(l+1) - \frac{m^2}{1-x^2} \right\} P_l^m(x) = 0, \quad (10.23)$$

of which the solution is the associated Legendre function $P_l^m(x)$.

11. Eigenfunctions for the Rigid Rotator.—It was postulated in Section 9c that the eigenfunction for the rigid rotator could be expressed as the product of two functions $Y(\theta)$ and $Z(\phi)$. The latter has been already evaluated, in the form of equation (9.39), and the former may be obtained by solving equation (9.50). Inserting the value of β given by equation (9.66), equation (9.50) becomes

$$\frac{d}{dx} \left\{ (1 - x^2) \frac{dY}{dx} \right\} + \left\{ l(l+1) - \frac{m^2}{1-x^2} \right\} Y = 0, \quad (11.1)$$

and comparison with equation (10.23) shows that a solution of (9.50) is

$$Y = c P_l^m(x), \quad (11.2)$$

where c is a constant, which may be a normalization factor. Since x is equal to $\cos \theta$, by the definition of equation (9.44), it follows that the required solution for the evaluation of the eigenfunction of the rotator is

$$Y(\theta) = c P_l^m(\cos \theta). \quad (11.3)$$

It can be shown that, like the Legendre polynomials, the associated Legendre functions form an orthogonal set in the physically significant interval $-1 \leq x \leq 1$; that is,

$$\int_{-1}^1 P_k^m(x) P_l^m(x) dx = 0, \quad \text{for } k \neq l. \quad (11.4)$$

On the other hand, when k is equal to l ,

$$\int_{-1}^1 P_l^m(x) P_l^m(x) dx = \frac{2}{2l+1} \cdot \frac{(l+m)!}{(l-m)!}, \quad \text{for } k = l, \quad (11.5)$$

and hence the normalization factor is given by

$$c = \sqrt{\frac{2l+1}{2} \cdot \frac{(l-m)!}{(l+m)!}}. \quad (11.6)$$

Inserting this value in equation (11.3) it is seen that

$$Y(\theta) = \sqrt{\frac{2l+1}{2} \cdot \frac{(l-m)!}{(l+m)!}} P_l^m(\cos \theta), \quad (11.7)$$

and consequently the required normalized eigenfunction for the rigid rotator, which is equal to $Y(\theta)Z(\phi)$, may be expressed as

$$\psi = \sqrt{\frac{2l+1}{4\pi} \cdot \frac{(l-m)!}{(l+m)!}} P_l^m(\cos \theta) e^{\pm im\phi}. \quad (11.8)$$

12. Degeneracy of Rotational States.—It can be seen from the definition of the Legendre polynomial [equation (10.15)] that the highest power of x is provided by the l th derivative of x^{2l} , and consequently it will involve x^l . It follows, therefore, that the m th derivative of $P_l(x)$, and hence also the associated Legendre function which involves this derivative, will become zero when m exceeds l . Consequently m , which as already seen must be zero or integral, can have only the series of values $0, 1, 2, \dots, l$, for a given value of l , if the eigenfunction of the rotator is to be finite. The term $e^{\pm im\phi}$ appearing in equation (11.8) implies that for each integral value of m there are two eigenfunctions, with m positive and negative respectively; hence, for a given l , the values of m can be $0, \pm 1, \pm 2, \dots, \pm l$. There are thus $2l+1$ possible values of m , and this same number of eigenfunctions represented by equation (11.8), for each value of l . It can be seen from equation (9.68) that the l 's determine the eigenstate of the rotator, and hence each energy state of a rigid rotator with free axis is $2l+1$ -fold degenerate. In other words, for every l value there are $2l+1$ states of the rigid rotator having the same, or almost the same, energy.

THE HYDROGEN-LIKE ATOM

13a. Hydrogen-Like Atoms: The Central Force Field Problem.—A hydrogen-like atom may be regarded as a system of two charged particles, the positively charged nucleus and the negatively charged electron, between which coulombic forces are operative. For a system of two or more particles the Schrödinger equation is most conveniently written in the form of equation (6.9), i.e.,

$$\mathbf{H}\psi = E\psi, \quad (13.1)$$

where ψ and E are the eigenfunction and energy, respectively, of the whole

system; the Hamiltonian operator \mathbf{H} is now defined by

$$\mathbf{H} = -\frac{h^2}{8\pi^2} \sum_i \frac{1}{m_i} \nabla_i^2 + V, \quad (13.2)$$

where m_i is the mass and ∇_i^2 is the Laplacian operator for the i th particle, the summation being made for all the particles constituting the given system. For the hydrogen-like atom, consisting of two particles, the Hamiltonian is given by

$$\mathbf{H} = -\frac{h^2}{8\pi^2} \left(\frac{1}{m_1} \nabla_1^2 + \frac{1}{m_2} \nabla_2^2 \right) + V, \quad (13.3)$$

where

$$\nabla_1^2 = \frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2} \quad \text{and} \quad \nabla_2^2 = \frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial y_2^2} + \frac{\partial^2}{\partial z_2^2}, \quad (13.4)$$

x_1, y_1 and z_1 being the coordinates of the particle of mass m_1 , and x_2, y_2 and z_2 are the coordinates of the other particle, of mass m_2 .

If ψ_T and E_T are used to represent the total eigenfunction and the total energy, respectively, for the whole system, then combination of equations (13.1) and (13.3) gives the wave equation for the system as

$$\frac{1}{m_1} \nabla_1^2 \psi_T + \frac{1}{m_2} \nabla_2^2 \psi_T + \frac{8\pi^2}{h^2} (E_T - V) \psi_T = 0. \quad (13.5)$$

The total eigenfunction ψ_T includes the contribution due to translational motion of the system as a whole, but this factor may be removed in the following manner. If it is supposed that ψ_T is a product of two eigenfunctions, namely ψ_t , which depends on the position of the center of mass of the system, and ψ , which is function only of the distance between the particles, then it is possible to show that

$$\nabla^2 \psi + \frac{8\pi^2 \mu}{h^2} (E - V) \psi = 0, \quad (13.6)$$

that is,

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 \mu}{h^2} (E - V) \psi = 0, \quad (13.7)$$

where x, y and z are the coordinates of the center of mass of the system, E is the total energy exclusive of the translational energy, and μ is the reduced mass. Since the latter is defined by

$$\mu = \frac{m_1 m_2}{m_1 + m_2},$$

it is evident if m_1 is the mass of the nucleus and m_2 is that of the electron, that m_1 is much greater than m_2 , and consequently μ is approximately equal to the electronic mass m_2 .

The potential energy V is a function of the position of the two particles relative to one another, and is independent of the translational motion of the system as a whole. The wave equation (13.7) is thus seen to be identical with that for a single particle of mass μ , which is virtually that of the electron, in a field of potential V . Transforming to spherical coordinates, this equation becomes [cf. equation (9.20)]

$$\begin{aligned} \frac{1}{r^2} \cdot \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \cdot \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) \\ + \frac{1}{r^2 \sin^2 \theta} \cdot \frac{\partial^2 \psi}{\partial \phi^2} + \frac{8\pi^2\mu}{h^2} \{E - V(r)\} \psi = 0. \end{aligned} \quad (13.8)$$

For the central force field problem, such as that under consideration, the potential V depends only on the distance between the electron and the nucleus, and not on the angles θ and ϕ ; hence in equation (13.8), the potential is written as a function of r , namely, $V(r)$.

13b. Separation of Variables.—As in the solution of the problem of the rigid rotator, the first step in solving equation (13.8) is to attempt to separate the variables. The assumption is consequently made that the eigenfunction ψ , which is a function of r , θ and ϕ , can be expressed as the product of three functions, viz., $R(r)$, $Y(\theta)$ and $Z(\phi)$, each of which is a function of the one indicated variable; thus,

$$\psi(r, \theta, \phi) = R(r)Y(\theta)Z(\phi). \quad (13.9)$$

Making this substitution in equation (13.8) and multiplying through by $(r^2 \sin^2 \theta)/RYZ$, the result is

$$\begin{aligned} \frac{\sin^2 \theta}{R} \cdot \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{1}{Z} \cdot \frac{d^2 Z}{d\phi^2} + \frac{\sin \theta}{Y} \cdot \frac{d}{d\theta} \left(\sin \theta \frac{dY}{d\theta} \right) \\ + r^2 \sin^2 \theta \frac{8\pi^2\mu}{h^2} \{E - V(r)\} = 0. \end{aligned} \quad (13.10)$$

In this expression, the second term is a function of the variable ϕ only, and hence it can be shown, by an argument similar to that used in Section 9c in connection with the rigid rotator problem, that this term must be a constant. Representing the constant by $-m^2$, it is possible to write

$$\frac{1}{Z} \cdot \frac{d^2 Z}{d\phi^2} = -m^2, \quad (13.11)$$

or

$$\frac{d^2 Z}{d\phi^2} + m^2 Z = 0, \quad (13.12)$$

these equations being identical with equations (9.29) and (9.30), respectively. Insertion of the value $-m^2$ in place of the second term in equation (13.10)

now gives

$$\frac{\sin^2 \theta}{R} \cdot \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) - m^2 + \frac{\sin \theta}{Y} \cdot \frac{d}{d\theta} \left(\sin \theta \frac{dY}{d\theta} \right) + r^2 \sin^2 \theta \frac{8\pi^2 \mu}{h^2} \{E - V(r)\} = 0, \quad (13.13)$$

and if this is divided through by $\sin^2 \theta$, the result, after rearrangement, is

$$\frac{1}{R} \cdot \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + r^2 \frac{8\pi^2 \mu}{h^2} \{E - V(r)\} = \frac{m^2}{\sin^2 \theta} - \frac{1}{Y \sin \theta} \cdot \frac{d}{d\theta} \left(\sin \theta \frac{dY}{d\theta} \right). \quad (13.14)$$

The left-hand side of this equation is seen to be dependent on the variable r only, while the right-hand side involves the variable θ only; it can be shown, therefore, by familiar arguments, that each side is constant. Setting each equal to β , there result the two equations

$$\frac{1}{\sin \theta} \cdot \frac{d}{d\theta} \left(\sin \theta \frac{dY}{d\theta} \right) + \left(\beta - \frac{m^2}{\sin^2 \theta} \right) Y = 0 \quad (13.15)$$

and

$$\frac{1}{r^2} \cdot \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) - \frac{\beta}{r^2} R + \frac{8\pi^2 \mu}{h^2} \{E - V(r)\} R = 0. \quad (13.16)$$

13c. Spherical Eigenfunctions.—It will now be apparent that the wave equation (13.8) has been separated into three equations, namely (13.12), (13.15) and (13.16), each of which involves but one variable, viz, ϕ , θ and r , respectively. It remains, therefore, to solve each of these equations individually. Equations (13.12) and (13.15) are identical with equations (9.30) and (9.43), respectively, for the rigid rotator, and hence it follows that, as for the latter, the solutions are given by the normalized eigenfunctions

$$Z(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi}, \quad (13.17)$$

where

$$m = 0, \pm 1, \pm 2, \dots, \pm l,$$

(see Section 12) the positive and negative values representing different possible solutions, and

$$Y(\theta) = \sqrt{\frac{2l+1}{2} \cdot \frac{(l-m)!}{(l+m)!}} P_l^m(\cos \theta), \quad (13.18)$$

as given by equations (9.39) and (11.7). The functions $Y(\theta)$ and $Z(\phi)$ are referred to as the *spherical eigenfunctions*, since they give the spherical, as distinct from the radial, distribution of the electron. As shown previously,

$Z(\phi)$ can be expressed, if desired, as a real rather than as a complex quantity [equation (9.42)].

The value of β in equation (13.15) is similar to that derived for the rigid rotator, and hence for the present case

$$\beta = l(l + 1), \quad (13.19)$$

where

$$l = 0, 1, 2, \dots$$

Further, as indicated above, if the eigenfunctions are to be finite, the integral value of m cannot exceed l .

13d. Laguerre Polynomials.—In order to complete the solution of the problem of the hydrogen-like atom it is necessary to consider equation (13.16), generally known as the *radial equation*, since it is a function of the radius vector r only. For this purpose it is required to have some knowledge of the Laguerre polynomials, and this subject will be treated first. These polynomials may be defined by utilizing the function

$$y = x^k e^{-x}, \quad (13.20)$$

which, differentiated k times, gives

$$\frac{d^k y}{dx^k} = \frac{d^k (x^k e^{-x})}{dx^k} \quad (13.21)$$

$$= e^{-x} L_k(x), \quad (13.22)$$

where $L_k(x)$ is the *Laguerre polynomial* in x of degree k ; hence it is possible to write the definition

$$L_k(x) = e^x \frac{d^k (x^k e^{-x})}{dx^k}. \quad (13.23)$$

By taking the p th derivative of this function there is obtained the *associated Laguerre polynomial* of degree $k - p$ and order p ; thus,

$$L_k^p(x) = \frac{d^p L_k(x)}{dx^p}. \quad (13.24)$$

From an examination of the expression defining $L_k(x)$, the Laguerre polynomial of degree k , it will be found that the highest power of x , which determines the degree of the polynomial, is x^k . Consequently, the highest power of x in the associated Laguerre polynomial $L_k^p(x)$, of degree $k - p$, is seen to be x^{k-p} . It follows, therefore, that p must always be less than or equal to k if the associated polynomial is to be different from zero. When p is equal to k the associated Laguerre polynomial, i.e., $L_k^k(x)$, contains no x terms; subsequent members of the series, i.e., with p greater than k , must therefore be zero.

For present purposes it is desired to find the differential equation that is satisfied by the Laguerre polynomials. Consider the equation

$$x \frac{dy}{dx} + (x - k)y = 0, \quad (13.25)$$

for which a possible solution is

$$y = x^k e^{-x}. \quad (13.26)$$

Upon differentiating equation (13.25), $k + 1$ times, the result is

$$x \frac{d^{k+2}y}{dx^{k+2}} + (x + 1) \frac{d^{k+1}y}{dx^{k+1}} + (k + 1) \frac{d^k y}{dx^k} = 0. \quad (13.27)$$

If a function u is defined by

$$u = \frac{d^k y}{dx^k}, \quad (13.28)$$

this function satisfies the equation

$$x \frac{d^2 u}{dx^2} + (x + 1) \frac{du}{dx} + (k + 1)u = 0. \quad (13.29)$$

In accordance with equations (13.22) and (13.28), it is seen that

$$u = e^{-x} L_k(x), \quad (13.30)$$

and hence

$$\frac{du}{dx} = e^{-x} \frac{dL_k(x)}{dx} - e^{-x} L_k(x), \quad (13.31)$$

and

$$\frac{d^2 u}{dx^2} = e^{-x} \frac{d^2 L_k(x)}{dx^2} - 2e^{-x} \frac{dL_k(x)}{dx} + e^{-x} L_k(x). \quad (13.32)$$

Substituting these values for u , du/dx and $d^2 u/dx^2$ in equation (13.29), this becomes

$$x \frac{d^2 L_k(x)}{dx^2} + (1 - x) \frac{dL_k(x)}{dx} + kL_k(x) = 0, \quad (13.33)$$

which is, consequently, the equation satisfied by the Laguerre polynomial $L_k(x)$. Differentiation of equation (13.33) p times gives

$$x \frac{d^{p+2} L_k(x)}{dx^{p+2}} + (p + 1 - x) \frac{d^{p+1} L_k(x)}{dx^{p+1}} + (k - p) \frac{d^p L_k(x)}{dx^p} = 0, \quad (13.34)$$

and if now the definition of the associated Laguerre polynomial, equation

(13.24), is introduced, it is seen that

$$x \frac{d^2 L_k^p(x)}{dx^2} + (p + 1 - x) \frac{dL_k^p(x)}{dx} + (k - p)L_k^p(x) = 0. \quad (13.35)$$

This equation is, therefore, the differential equation for which the associated Laguerre polynomial $L_k^p(x)$ is a solution.

13e. Solution of the Radial Equation.—Upon inserting the value of β , equal to $l(l + 1)$, into the radial equation (13.16) the latter becomes

$$\frac{1}{r^2} \cdot \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \left[-\frac{l(l + 1)}{r^2} + \frac{8\pi^2\mu}{h^2} \{E - V(r)\} \right] = 0, \quad (13.36)$$

or, expanding the first term,

$$\frac{d^2 R}{dr^2} + \frac{2}{r} \cdot \frac{dR}{dr} + \left[-\frac{l(l + 1)}{r^2} + \frac{8\pi^2\mu}{h^2} \{E - V(r)\} \right] = 0. \quad (13.37)$$

So far the treatment has been general, for any central force field, but for the case of particular interest, namely the hydrogen-like atom, it is possible to introduce an explicit expression for the potential function $V(r)$. The system consists of an electron of charge e moving in the central force field of a nucleus, of effective charge Ze , at a distance r .⁶ The value of $V(r)$ is thus given by

$$V(r) = -\frac{Ze^2}{r}, \quad (13.38)$$

and so equation (13.37) may be written as

$$\frac{d^2 R}{dr^2} + \frac{2}{r} \cdot \frac{dR}{dr} + \left\{ \frac{8\pi^2\mu E}{h^2} + \frac{8\pi^2\mu Ze^2}{h^2 r} - \frac{l(l + 1)}{r^2} \right\} R = 0. \quad (13.39)$$

In the subsequent treatment of this equation, it is necessary to distinguish between positive and negative values of E . According to classical atomic theory, negative values of E correspond to the nonionized atom with closed electronic shells, and this condition will be assumed to apply in the following quantum mechanical discussion. With E negative, it is convenient to introduce a new parameter n defined by

$$n^2 = -\frac{2\pi^2\mu Ze^4}{h^2 E}, \quad (13.40)$$

as well as the new variable x in place of r , defined by

$$x = \frac{2Z}{na_0} r, \quad (13.41)$$

⁶ The letter Z representing the effective number of charges on the nucleus will, of course, not be confused with the same letter used earlier to represent a function of ϕ .

where

$$a_0 = \frac{\hbar^2}{4\pi^2\mu e^2}. \quad (13.42)$$

It will be observed that the quantity a_0 is identical with the so-called Bohr orbit of the hydrogen atom, that is, the smallest orbit of the normal hydrogen atom as given by the Bohr theory.

Introduction of the values of n and x into equation (13.39), and the replacement of $R(r)$ by the new function $X(x)$, leads to

$$\frac{d^2X}{dx^2} + \frac{2}{x} \cdot \frac{dX}{dx} + \left\{ -\frac{1}{4} + \frac{n}{x} - \frac{l(l+1)}{x^2} \right\} X = 0, \quad (13.43)$$

where the physically significant limits of x correspond to those of r , namely zero to infinity. An indication of the solution of this equation may be obtained by taking x very large, so that the corresponding asymptotic equation is

$$\frac{d^2X}{dx^2} - \frac{1}{4} X = 0, \quad (13.44)$$

for which the solutions are

$$X(x) = e^{x/2} \quad \text{and} \quad X(x) = e^{-x/2}. \quad (13.45)$$

Since x may vary from zero to infinity, the former of these solutions will increase as x increases; this will lead, as seen in other cases, to an unacceptable wave function. On the other hand, the second solution will be satisfactory, since it decreases to zero as x —and hence r , the distance of the electron from the nucleus—increases to infinity.

Bearing in mind the asymptotic solution, a possible solution to equation (13.43) is thus

$$X(x) = e^{-x/2} F(x), \quad (13.46)$$

where $F(x)$ is another function of the variable x . From various considerations it appears that $F(x)$ may be split into two factors, viz., x^l , where l has the same significance as in equation (13.43) and previous equations, and another function of x , namely $G(x)$; hence it is possible to write

$$\begin{aligned} R(r) &= X(x) \\ &= e^{-x/2} x^l G(x). \end{aligned} \quad (13.47)$$

From this relationship d^2X/dx^2 and dX/dx can be evaluated in terms of $G(x)$ in the usual manner; if the results are substituted in equation (13.43), there is obtained

$$x \frac{d^2G}{dx^2} + \{(2l+1) + 1 - x\} \frac{dG}{dx} + (n - l - 1)G = 0. \quad (13.48)$$

Comparison of this equation with equation (13.35) shows that $G(x)$ may

be identified with the associated Laguerre polynomial $L_k^p(x)$, with

$$p = 2l + 1 \quad (13.49)$$

and

$$k = n + l. \quad (13.50)$$

This polynomial or, more correctly, the polynomial multiplied by a constant factor, will thus be a solution of equation (13.48), so that it is possible to write

$$G(x) = CL_{n+l}^{2l+1}(x), \quad (13.51)$$

where C is a constant which may be made equal to the normalization factor. The complete expression for the function $R(r)$ is thus seen from equation (13.47) to be given by

$$R(r) = Ce^{-x/2} x^l L_{n+l}^{2l+1}(x). \quad (13.52)$$

This is clearly an acceptable function, for the associated Laguerre polynomial, as already seen, has a finite number of terms only.

13f. Atomic Energy Levels and Quantum Numbers.—Before proceeding to normalize the radial function $R(r)$ and to derive the complete eigenfunction for the hydrogen-like atom, important results may be obtained concerning the permitted energy levels of this system. In the associated Laguerre polynomial $L_k^p(x)$, which is an acceptable solution of equation (13.48), both p and k must be zero or integral. Utilizing the equivalent values of p and k given by equations (13.49) and (13.50), viz., $2l + 1$ and $n + l$, respectively, it follows that $2l + 1$ and $n + l$ must be zero or integral. It has been previously established that l must be zero or integral, and since p is less than or equal to k (Section 13d), it follows that

$$n = 1, 2, 3, \dots \quad (13.53)$$

It follows, therefore, from the definition of n given by equation (13.40), that the eigenvalues E_n of the energy for the case under consideration are represented by the expression

$$E_n = -\frac{2\pi^2\mu Z^2 e^4}{n^2 h^2}. \quad (13.54)$$

where n is integral or zero. This result is the same as that obtained by Bohr for the energy levels of a hydrogen-like atom, utilizing the older quantum theory and certain postulates concerning the quantization of the angular momentum of the electron. It is seen, therefore, that the acceptable solutions of the wave equation lead to permitted energy values which are the same as those derived from the Bohr theory. The integral nature of n , which can now be identified with the *principal quantum number* (see Section 1a) of the atom, is clearly a necessary condition for the acceptable solution, rather than a postulate, as in the Bohr treatment.

By making use of the condition referred to in Section 13d that k must be greater than or equal to p , it is possible to establish a relationship between the permitted values of n and l . Since $k \geq p$, it follows, using equations (13.49) and (13.50), that

$$\begin{aligned} n + l &\geq 2l + 1, \\ \therefore l &\leq n - 1. \end{aligned} \quad (13.55)$$

Although the principal quantum number n may, theoretically, be zero, this value has no physical significance, for it would make E_n numerically equal to infinity. The possible values of n are thus 1, 2, 3, \dots , and hence it follows by equation (13.55) that l , which is the equivalent of the *azimuthal quantum number*, can be 0, 1, 2, \dots , $n - 1$.

It has been seen in connection with the problem of the rigid rotator that the possible values of m are 0, ± 1 , ± 2 , \dots , $\pm l$, and the same conditions apply to the present case, as indicated in Section 13c. Provided there is no perturbing field, these $2l + 1$ values correspond to the same energy, but in a magnetic field the levels are separated and $2l + 1$ different orientations are possible. The zero or integral m is thus the equivalent of the *magnetic quantum number* of atomic structural theory (Section 1a). Wave mechanics thus provides a satisfactory basis for the occurrence of the three integral quantum numbers n , l and m ; the problem of the spin quantum number will be taken up later.

13g. Normalized Hydrogen-Like Eigenfunctions.—The complete solution $\psi(r, \theta, \phi)$ of the wave equation for the hydrogen-like atom is obtained by multiplying the spherical eigenfunctions $Y(\theta)$ and $Z(\phi)$, which depend on the angles θ and ϕ , respectively, by the radial eigenfunction $R(r)$. The values of the two former, as given by equations (13.17) and (13.18), are already normalized, but this still remains to be done for $R(r)$ by giving an appropriate value to the constant C in equation (13.52). The normalizing condition, for the physically significant interval of zero to infinity, is

$$\int_0^\infty R(r)R^*(r)r^2dr = 1, \quad (13.56)$$

the factor r^2 being necessary to convert the length dr into an element of volume. Introduction of the values of $R(r)$ and of $R^*(r)$, which are identical in this case, leads to the result

$$C = \sqrt{\left(\frac{x}{r}\right)^3 \frac{(n-l-1)!}{2n\{(n+l)!\}^3}}. \quad (13.57)$$

Inserting this value in equation (13.52) and making use of the definition of x given by equation (13.41), it follows that the normalized radial part of the eigenfunction for a hydrogen-like atom is

$$R_{nl}(r) = \sqrt{\left(\frac{2Z}{na_0}\right)^3 \frac{(n-l-1)!}{2n\{(n+l)!\}^3}} e^{-Zr/na_0} \left(\frac{2Zr}{na_0}\right)^l L_{n+l}^{2l+1}\left(\frac{2Zr}{na_0}\right). \quad (13.58)$$

The subscript nl has been added to indicate that this function involves the quantum numbers n and l . Similarly $Y_{lm}(\theta)$ depends on l and m , while $Z_m(\phi)$ contains m only; these two functions are repeated here for the sake of completeness; thus

$$Y_{lm}(\theta) = \sqrt{\frac{2l+1}{2} \cdot \frac{(l-m)!}{(l+m)!}} P_l^m(\cos \theta) \quad (13.59)$$

and

$$Z_m(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi}. \quad (13.60)$$

Finally the complete eigenfunction, exclusive of spin, is given by

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r) Y_{lm}(\theta) Z_m(\phi). \quad (13.61)$$

Although these functions appear to be very complicated, they actually reduce to relatively simple forms, especially for low values of the quantum numbers n , l and m . As these are the cases of immediate interest, the expressions for $R(r)$, $Y(\theta)$ and $Z(\phi)$ for $n = 1$ and 2 , for $l = 1$ and 0 , and for m (i.e., m_l) $= 0$ and ± 1 , are given in Tables II and III. Since equally good

TABLE II. NORMALIZED RADIAL FUNCTIONS FOR HYDROGEN-LIKE ATOMS

n	l	$R_{nl}(r)$
1	0	$2 \left(\frac{Z}{a_0} \right)^{3/2} e^{-Zr/a_0}$
2	0	$\frac{1}{2\sqrt{2}} \left(\frac{Z}{a_0} \right)^{3/2} \left(2 - \frac{Zr}{a_0} \right) e^{-Zr/2a_0}$
2	1	$\frac{1}{2\sqrt{6}} \left(\frac{Z}{a_0} \right)^{3/2} \frac{Zr}{a_0} e^{-Zr/2a_0}$

TABLE III. NORMALIZED SPHERICAL FUNCTIONS FOR HYDROGEN-LIKE ATOMS

l	m	$Y_{lm}(\theta)$	$Z_m(\phi)$
0	0	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2\pi}}$
1	0	$\sqrt{\frac{3}{2}} \cos \theta$	$\frac{1}{\sqrt{2\pi}}$
1	± 1	$\frac{\sqrt{3}}{2} \sin \theta$	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$ or $\frac{1}{\sqrt{\pi}} \cos \phi$ and $\frac{1}{\sqrt{\pi}} \sin \phi$

normalized eigenfunctions may be obtained by reversing the signs preceding the functions, this change has been made in Table II for the sake of convenience. In Table III, both the complex and real values of the eigenfunction $Z_m(\phi)$ are given for m equal to ± 1 .

The real forms of the complete eigenfunctions, exclusive of spin, for hydrogen-like atoms with the electron in either the K shell ($n = 1$) or the L shell ($n = 2$) are given in Table IV. In accordance with the limitations

TABLE IV. COMPLETE EIGENFUNCTIONS FOR HYDROGEN-LIKE ATOMS

n	l	m	State	Eigenfunction
1	0	0	1s	$\psi_{100} = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0} \right)^{3/2} e^{-Zr/a_0}$
2	0	0	2s	$\psi_{200} = \frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a_0} \right)^{3/2} \left(2 - \frac{Zr}{a_0} \right) e^{-Zr/2a_0}$
2	1	0	2p	$\psi_{210} = \frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a_0} \right)^{5/2} e^{-Zr/2a_0} \cos \theta$
2	1	± 1	2p	$\psi_{211} = \begin{cases} \frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a_0} \right)^{5/2} e^{-Zr/2a_0} \sin \theta \cos \phi \\ \frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a_0} \right)^{5/2} e^{-Zr/2a_0} \sin \theta \sin \phi \end{cases}$

on the values of l and m , the only possibility for $n = 1$ is $l = 0$ and $m = 0$, the electron being then described by the symbol 1s (see Section 1a). When n is 2, there are four possible electronic states, namely $l = 0$, $m = 0$, designated 2s, and $l = 1$, $m = 1, 0, -1$, which correspond to the three possible 2p states.

The complete one-electron eigenfunctions, exclusive of spin, such as those recorded in Table IV, are the quantum mechanical equivalent of the classical electron orbits. For this reason they have been referred to as *orbitals*. In some cases they are called atomic orbitals, to distinguish them from the orbitals associated with molecules (see Section 16b).

13h. Eigenfunctions and Probability Distribution.—Although the radial parts of the wave functions are not of great chemical importance, brief reference will be made to them as they serve to indicate the essential difference between the new quantum mechanics and the older quantum theory as used by Bohr. The value of the square of the radial function—this is the same as the square of the absolute value, since $R(r)$ is real—is a measure of the probability of finding the electron in an element of unit length at a distance r from the nucleus. According to classical theory, which required the electron to be confined to a definite orbit, this probability should be zero at all distances except that representing the position of the orbit. The radial

functions of quantum mechanics, such as those given in Table II, however, lead to quite different conclusions. There is generally a finite probability of finding the electron at all distances from the nucleus from zero to infinity; as is to be expected, this probability falls off rapidly to very small values when r is large. Instead of studying $R(r)^2$, which gives the probability of finding an electron in a unit length, a more useful property, known as the *distribution function*, is $4\pi r^2 R(r)^2$, which is a measure of the probability that the electron will be found in a spherical shell at a distance r from the nucleus. Some examples of the shape of this distribution function are given in Fig. 5.

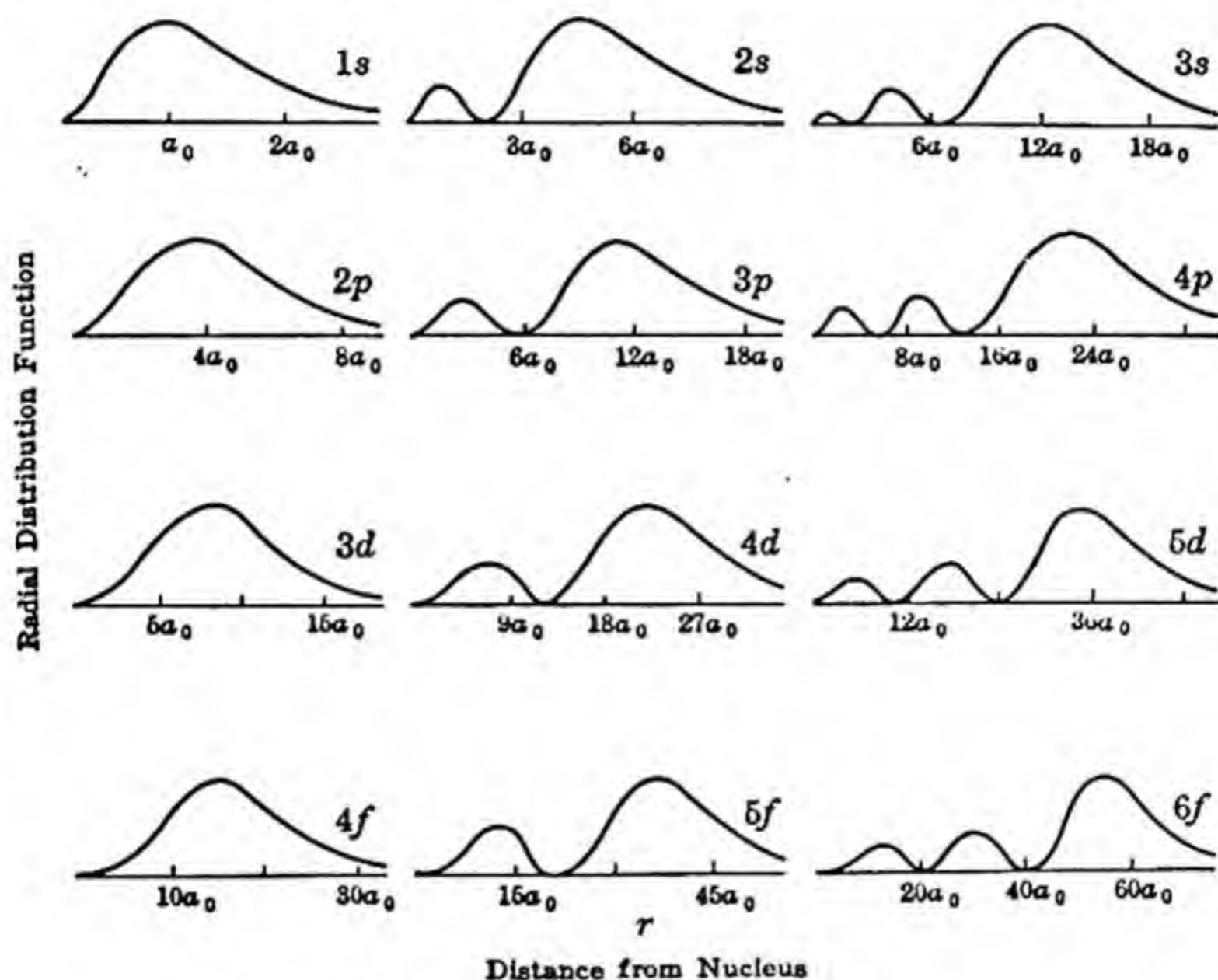


FIG. 5. Radial distribution function

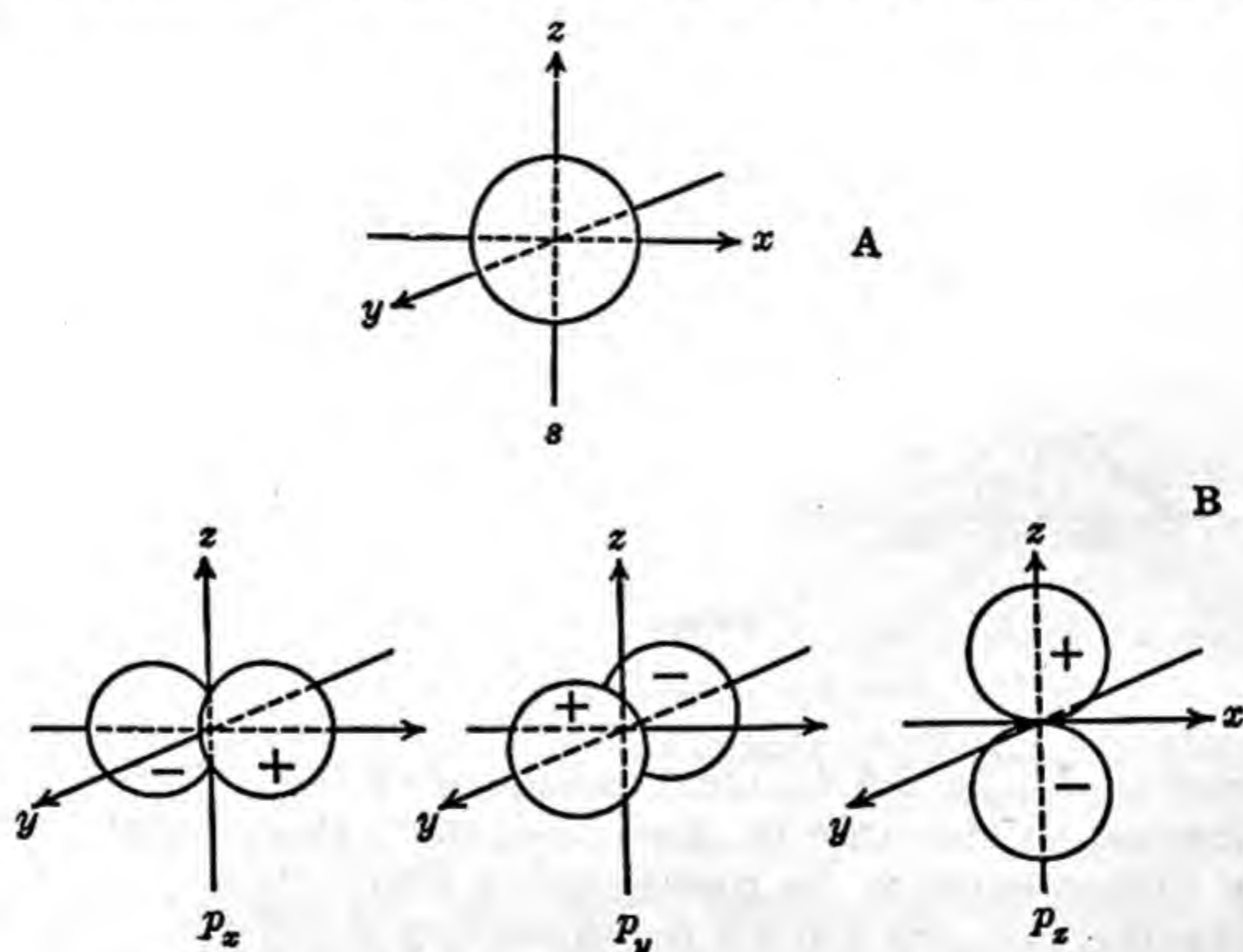
The curves for $1s$, $2p$, $3d$, $4f$, etc. electrons show one maximum only, and it is of interest to note that in these cases the maxima occur at distances from the nucleus equal to the corresponding Bohr orbits.

As a general rule, the s and p eigenfunctions ($l = 0$ and 1) for the same value of n , e.g., ψ_{200} , ψ_{210} and ψ_{211} , show *approximately* the same dependence on r , and the difference between these eigenfunctions lies essentially in their dependence on the angles θ and ϕ ; that is to say, the radial parts of the eigenfunctions are approximately the same, but the spherical parts differ appreciably. It is this fact which is of fundamental importance to the quantum mechanical theory of valence, as will be seen in Section 20a. By combining the values for $Y_{lm}(\theta)$ with the real values of $Z_m(\phi)$ given in Table III, the complete spherical wave functions for s and p electrons in hydrogen-like atoms may be readily determined. These are recorded in Table V; for

TABLE V. NORMALIZED COMPLETE SPHERICAL EIGENFUNCTIONS $Y_{lm}(\theta)Z_m(\phi)$

l	m	Symbol	Eigenfunction	Normalized to 4π
0	0	s	$\frac{1}{\sqrt{4\pi}}$	1
1	0	p_z	$\sqrt{\frac{3}{4\pi}} \cos \theta$	$\sqrt{3} \cos \theta$
1	-1	p_y	$\sqrt{\frac{3}{4\pi}} \sin \theta \sin \phi$	$\sqrt{3} \sin \theta \sin \phi$
1	1	p_x	$\sqrt{\frac{3}{4\pi}} \sin \theta \cos \phi$	$\sqrt{3} \sin \theta \cos \phi$

reasons which will appear shortly, the three p eigenfunctions are distinguished by the subscript x , y and z , respectively.⁷ The values given in the fourth column are normalized to unity in the ordinary way. For subsequent pur-

FIG. 6. Spherical s and p eigenfunctions

poses it is convenient to make the s eigenfunction equal to unity, and so the results are normalized to 4π in the final column of Table V. It should be noted that the results in this table are applicable to any s and p electrons

⁷ It will be seen in Section 40a that electron orbitals for which m (or m_l) is 0 and 1, respectively, are designated by the symbols σ and π , respectively, when they are involved in the formation of molecules. These three p eigenfunctions are consequently represented as $p\sigma$, $p\pi_-$ and $p\pi_+$, for m equal to 0, -1 and +1, respectively.

in hydrogen-like atoms, irrespective of the value of the principal quantum number, since the latter does not appear in the spherical parts of the eigenfunctions.

Consideration of the data recorded in Table V brings to light a number of significant points. In the first place, the s function is seen to be independent of the angles θ and ϕ ; it is consequently spherically symmetrical, as indicated in Fig. 6 A. The p eigenfunctions, however, exhibit an interesting angular distribution; it can be shown that p_x , p_y and p_z are identical in form, consisting of two spheres (one positive and one negative) in contact, somewhat like a dumbbell. The three sets of double spheres are, however, oriented along the x , y and z axes, respectively, that is, in three directions at right angles to each other (Fig. 6 B). The relative magnitude of the s eigenfunction, as given by the last column in Table V, is unity in every

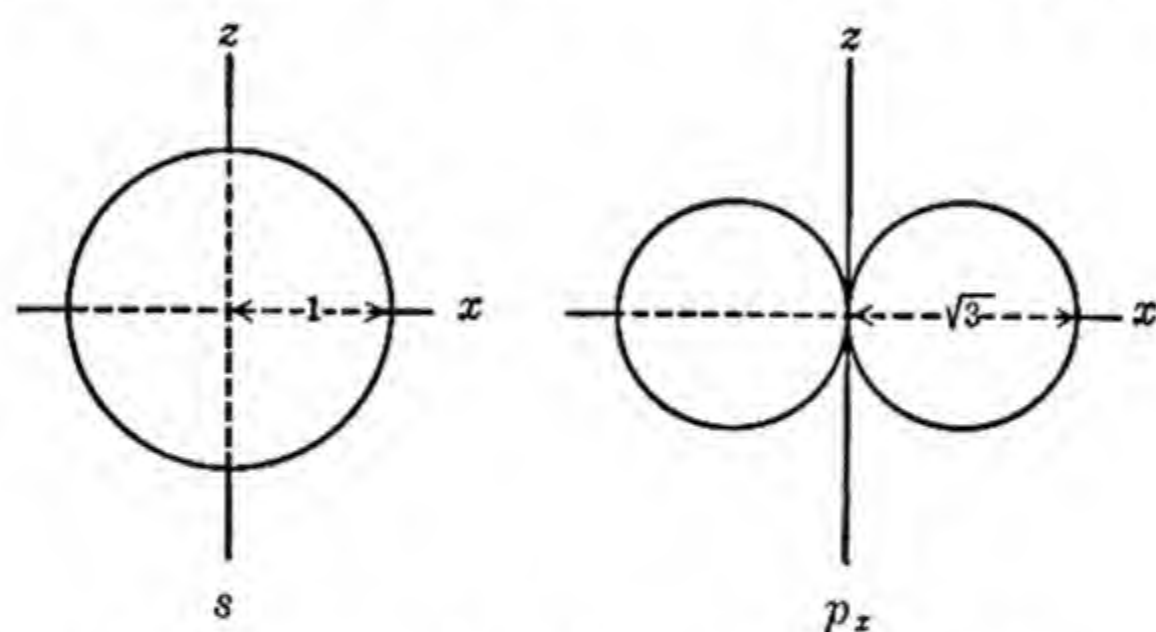


FIG. 7. Sections of spherical s and p eigenfunctions

direction. On the other hand, the corresponding values for the p functions are largest in certain directions, and the magnitudes of the maximum values may be derived by setting $\sin \theta$, $\cos \theta$, $\sin \phi$ and $\cos \phi$ equal to unity. It is seen that the maxima of p_x , p_y and p_z are each equal to $\sqrt{3}$. The maximum value of the spherical p eigenfunction is thus $\sqrt{3}$ times as great as that of the s function; this is shown by the sections in the xz plane drawn in Fig. 7. The foregoing conclusions may be summarized in the following manner. The probability of finding an s electron is the same in all directions around the nucleus of a hydrogen-like atom, but a p electron will tend to concentrate in certain preferred directions. These directions are at right angles to each other for the three types of p electrons in the atom. Finally, the maximum probability of the p electron being in one of these preferred directions is $\sqrt{3}$ times as great as that of an s electron being in any direction. Further reference to these matters will be made in Section 20c.

CHAPTER III

QUANTUM THEORY OF VALENCE ¹

THE VARIATION METHOD

14a. Approximation Methods.—The exact solution of the wave equation, such as that carried out in the previous chapter for the hydrogen-like atom, is possible only when the system contains a single electron. If several electrons are involved, as is the case in most problems of chemical interest, it is not feasible to obtain a complete solution of the wave equations. In these circumstances the best that can be done is to employ an approximate procedure, and several methods have been suggested, of which two have been most widely employed. These are the *perturbation method* and the *variation method*. For the problems of immediate interest the two procedures lead to virtually the same result, and as the theory of the latter method is simpler, this will be given in detail while the perturbation method will be referred to very briefly.

14b. The Perturbation Method.—The perturbation theory is based on the supposition that an actual problem can be treated as a slight modification, or perturbation, of an ideal problem which is capable of exact solution. If the actual Schrödinger equation which must be solved is

$$\mathbf{H}\psi = E\psi, \quad (14.1)$$

then it is supposed that a complete solution is available for the equation

$$\mathbf{H}_0\psi_0 = E_0\psi_0 \quad (14.2)$$

of an unperturbed system whose Hamiltonian operator \mathbf{H}_0 differs only slightly from that (\mathbf{H}) in the problem under consideration. The two Hamiltonians are assumed to be related by the equation

$$\mathbf{H} = \mathbf{H}_0 + \lambda\mathbf{H}' \quad (14.3)$$

where λ is an arbitrary parameter; the quantity $\lambda\mathbf{H}'$ is called the *perturbation term*. Substitution for \mathbf{H} in equation (14.1) then gives

$$(\mathbf{H}_0 + \lambda\mathbf{H}')\psi = E\psi, \quad (14.4)$$

and this is the equation which has to be solved. The method of solution depends on whether the system is degenerate or not, but the treatment will not be given here because of its relative complexity.

¹ Dushman, "The Elements of Quantum Mechanics"; Hellmann, "Einführung in die Quantenchemie"; Pauling and Wilson, "Introduction to Quantum Mechanics"; Penney, "The Quantum Theory of Valency"; Van Vleck and Sherman, *Rev. Mod. Phys.*, 7, 167 (1935).

14c. The Variation Method.²—The equations required for the present purpose can be obtained equally well by the use of the variation treatment in the following manner. As seen in Section 5b, an arbitrary function ψ , assumed to be of the proper type, can be expanded in terms of a normalized, orthogonal set of functions, ϕ_i ; thus,

$$\psi = c_1\phi_1 + c_2\phi_2 + \cdots + c_i\phi_i + \cdots \quad (14.5)$$

$$= \sum_i c_i\phi_i, \quad (14.6)$$

where

$$c_i = \int \phi_i^* \psi d\tau. \quad (14.7)$$

If ψ is normalized, then, by equation (5.9),

$$c_1c_1^* + c_2c_2^* + \cdots + c_ic_i^* + \cdots = 1$$

that is,

$$\sum_i c_ic_i^* = 1. \quad (14.8)$$

If the functions ϕ_i are suitable eigenfunctions for the Hamiltonian operator, then the appropriate form of the Schrodinger equation is

$$\mathbf{H}\phi_i = E_i\phi_i. \quad (14.9)$$

Upon multiplying both sides by ϕ_i^* and integrating the result over the configuration space, it is seen that

$$\begin{aligned} \int \phi_i^* \mathbf{H}\phi_i d\tau &= E_i \int \phi_i^* \phi_i d\tau, \\ \therefore E_i &= \frac{\int \phi_i^* \mathbf{H}\phi_i d\tau}{\int \phi_i^* \phi_i d\tau}, \end{aligned} \quad (14.10)$$

or

$$E_i = \int \phi_i^* \mathbf{H}\phi_i d\tau, \quad (14.11)$$

since the eigenfunctions ϕ_i are assumed to be normalized.

Consider now the corresponding integral involving ψ , i.e., $\int \psi^* \mathbf{H}\psi d\tau$, which is represented by the letter E ; utilizing equation (14.6), it follows that

$$E = \int \psi^* \mathbf{H}\psi d\tau = \sum c_ic_i^* \int \phi_i^* \mathbf{H}\phi_i d\tau, \quad (14.12)$$

² Glasstone, Laidler and Eyring, "The Theory of Rate Processes," p. 62 et seq.

and hence, by equation (14.11),

$$E = \sum c_i c_i^* E_i. \quad (14.13)$$

Suppose E_0 is the actual lowest energy value for a given system; then, taking into consideration equation (14.8), subtraction of E_0 from both sides of equation (14.13) gives

$$E - E_0 = \sum c_i c_i^* (E_i - E_0). \quad (14.14)$$

Since E_0 is the lowest possible value of the energy, $E_i - E_0$ must be positive or zero for all values of i ; further, since $c_i c_i^*$ is also always positive or zero, it is seen that the right-hand side of equation (14.14) must similarly be positive or zero. It follows, therefore, that

$$E - E_0 \geq 0,$$

or

$$E \geq E_0, \quad (14.15)$$

and hence by the definition of E ,

$$\int \psi^* \mathbf{H} \psi d\tau \geq E_0. \quad (14.16)$$

Since ψ has been chosen quite arbitrarily, it follows that no matter what form of ψ is postulated, provided it is suitable for the present problem, the integral represented by the left-hand side of equation (14.16) can never be less than the true minimum energy of the system. By varying the function ψ —the so-called *variation function*—in the proper manner, it will then be possible to obtain a value for the integral which approximates the true energy very closely.

Suppose the variation function ψ can be expressed as the sum of a set of linearly independent functions χ ; thus,

$$\psi = a_1 \chi_1 + a_2 \chi_2 + \cdots + a_i \chi_i + \cdots + a_n \chi_n, \quad (14.17)$$

in which the independent parameters $a_1, a_2, \cdots, a_i, \cdots, a_n$, have to be varied so as to give a value of E in best agreement with the actual energy. The functions χ are supposed to be of the well-behaved type (Section 4d), and it will be assumed, although this is not strictly necessary, that they are normalized. Consider the integral I , defined by

$$I = \int \psi^* (\mathbf{H} - E) \psi d\tau. \quad (14.18)$$

If ψ and E are the correct eigenfunction and energy of the system, respectively, then

$$\mathbf{H}\psi = E\psi,$$

or

$$(\mathbf{H} - E)\psi = 0, \quad (14.19)$$

so that the integral I will then be zero. If the functions χ in equation (14.17) constitute a complete set, variation of the parameters so as to make I zero would then give the correct values of ψ and E . Even if the set is not complete, however, it is still possible to obtain a best value of E , according to the variation theorem, by suitable choice of the parameters.

Since the lowest value of the integral $\int \psi^* \mathbf{H} \psi d\tau$ approximates most closely to the actual energy, as seen above, it follows that even if the integral I is not zero, its lowest value, at least, will correspond to the best value of the energy. The condition that I should be a minimum is given by

$$dI = \frac{\partial I}{\partial a_1} da_1 + \frac{\partial I}{\partial a_2} da_2 + \cdots + \frac{\partial I}{\partial a_n} da_n = 0, \quad (14.20)$$

and if da_1, da_2, \dots, da_n are independent and not zero, then I will be a minimum only when

$$\frac{\partial I}{\partial a_1} = \frac{\partial I}{\partial a_2} = \cdots = \frac{\partial I}{\partial a_n} = 0. \quad (14.21)$$

Inserting the values of ψ and ψ^* obtained from equation (14.17) into the definition of I , equation (14.18), it is seen that

$$I = \int \sum_i a_i^* \chi_i^* (\mathbf{H} - E) \sum_j a_j \chi_j d\tau, \quad (14.22)$$

and since $\partial I / \partial a_1 = 0$, by equation (14.21), it follows that

$$\sum_{j=1}^n a_j \left(\int \chi_1^* \mathbf{H} \chi_j d\tau - E \int \chi_1^* \chi_j d\tau \right) = 0. \quad (14.23)$$

By the use of certain recognized abbreviations, the appearance of equation (14.23) may be simplified; these are H_{ij} , referred to as the *matrix component* (or *matrix element*) of the operator \mathbf{H} between the eigenfunctions χ_i and χ_j , defined by

$$H_{ij} = \int \chi_i^* \mathbf{H} \chi_j d\tau, \quad (14.24)$$

and Δ_{ij} , the matrix component of unity, defined by

$$\Delta_{ij} = \int \chi_i^* \chi_j d\tau. \quad (14.25)$$

Using these symbols, equation (14.23) becomes

$$\sum_{j=1}^n a_j (H_{1j} - \Delta_{1j} E) = 0 \quad (14.26)$$

It will be recalled that this result was obtained on differentiation of I , given by equation (14.22), with respect to a_1 and equating the result to zero; a set of n similar equations, represented by

$$\sum_{j=1}^n a_j (H_{kj} - \Delta_{kj} E) = 0, \quad \text{where} \quad k = 1, 2, \dots, n, \quad (14.27)$$

can be obtained on differentiation with respect to a_1, a_2, \dots, a_n , and equating to zero in each case, in accordance with equation (14.21).

The expression in equation (14.27) represents a set of n simultaneous, homogeneous, linear equations in the n independent variables a_1, a_2, \dots, a_n , and if this set is to have nontrivial solutions, i.e., different from zero, the determinant of the coefficients must vanish. It follows, therefore, that the necessary condition is

$$\begin{vmatrix} H_{11} - \Delta_{11}E & H_{12} - \Delta_{12}E & \cdots & H_{1n} - \Delta_{1n}E \\ H_{21} - \Delta_{21}E & H_{22} - \Delta_{22}E & \cdots & H_{2n} - \Delta_{2n}E \\ \vdots & \vdots & & \vdots \\ \vdots & \vdots & & \vdots \\ H_{n1} - \Delta_{n1}E & H_{n2} - \Delta_{n2}E & \cdots & H_{nn} - \Delta_{nn}E \end{vmatrix} = 0. \quad (14.28)$$

This equation, which is of the n th degree in E , is frequently referred to as the *secular equation* of the particular problem being studied. Every H_{ij} and Δ_{ij} has a definite numerical value, and so the equation can be solved, in principle, to give n roots, viz., E_1, E_2, \dots, E_n . The lowest root of this set will then approximate most closely to the true energy of the system. The better the variation function, given by equation (14.17), the more nearly will these values approach each other.

Having found the lowest root of the secular equation, it is now possible to determine the appropriate values of the parameters a_1, a_2, \dots, a_n in equation (14.17). This particular root is inserted in the n equations represented by (14.27), and if the first $n - 1$ of these equations are divided by a_n , it is possible to solve explicitly for the $n - 1$ ratios $a_1/a_n, a_2/a_n, \dots, a_{n-1}/a_n$. This set of ratios, together with a normalizing condition, permits the evaluation of all the a 's, and so the form of the eigenfunction which gives the best value of the energy can be determined.

THE HYDROGEN MOLECULE

15a. The Heitler-London Method: Coulombic and Exchange Integrals.—

The first reasonably satisfactory quantum mechanical treatment of the hydrogen molecule was made by Heitler and London;³ apart from its intrinsic importance it has certain consequences of special interest for the theory of valence. The actual method employed by Heitler and London was based on the use of the perturbation theory, but the same results can be obtained by utilizing the equations derived by the variational method, as described in the previous section.

³ Heitler and London, *Z. Physik*, **44**, 455 (1927).

The hydrogen molecule consists of two positively charged nuclei, A and B, and two electrons designated by the numbers 1 and 2, as indicated in Fig. 8; the various distances involved in the molecule are shown in the figure. When the distance r_{AB} is large, the system under consideration becomes equivalent to two separated hydrogen atoms, and if these are in their normal (ground) states, the appropriate eigenfunctions (orbitals), exclusive of spin, will be the hydrogen-like $1s$ wave functions (ψ_{100}) given in Table IV, with Z equal to unity. These orbitals may be represented by $u_A(1)$ and $u_B(2)$, the suffixes A and B, and the numerals (1) and (2), implying that electron (1) is associated with nucleus A, and electron (2) with nucleus B. When the two normal hydrogen atoms are brought together to form a molecule, a reasonably simple eigenfunction would be the product of these two $1s$ atomic wave functions; thus

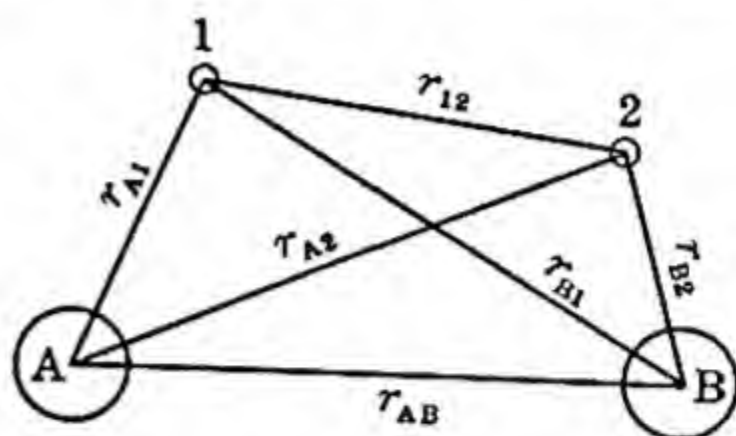


FIG. 8. The hydrogen molecule system

$$\psi_I = u_A(1)u_B(2). \quad (15.1)$$

If the two electrons were interchanged, so that electron (2) were associated with nucleus A and electron (1) with nucleus B, the atomic eigenfunctions would be $u_A(2)$ and $u_B(1)$, respectively. However, the complete system would not be affected by the exchange of electrons, and hence an equally good wave function for the hydrogen molecule would be

$$\psi_{II} = u_A(2)u_B(1). \quad (15.2)$$

Since there are two eigenfunctions corresponding to the same energy value of the hydrogen molecule, the system is two-fold degenerate, for relatively large interatomic distances.

In order to apply the variation treatment, a trial eigenfunction may be chosen of the form [cf. equation (14.17)]

$$\psi = a_1\psi_I + a_2\psi_{II}, \quad (15.3)$$

which is a linear combination of the two independent functions ψ_I and ψ_{II} . The secular equation for evaluating the corresponding energy E in the present case is therefore

$$\begin{vmatrix} H_{II} - \Delta_{II}E & H_{I II} - \Delta_{I II}E \\ H_{II I} - \Delta_{II I}E & H_{II II} - \Delta_{II II}E \end{vmatrix} = 0. \quad (15.4)$$

The matrix components H_{II} and $H_{II II}$ are defined by

$$H_{II} = \iint \psi_I \mathbf{H} \psi_I d\tau_1 d\tau_2 \quad (15.5)$$

and

$$H_{II II} = \int \int \psi_{II} \mathbf{H} \psi_{II} d\tau_1 d\tau_2, \quad (15.6)$$

where $d\tau_1$ and $d\tau_2$ refer to elements of the configuration spaces of the electrons (1) and (2), respectively. The eigenfunctions ψ_I and ψ_{II} are real, and so it is unnecessary to include the complex conjugates in the definitions of the matrix components. The integrals $H_{II I}$ and $H_{II II}$ are known as the *coulombic integrals*, for it will be seen later that they give the classical (coulombic) electronic interaction energy for the hydrogen molecule, taking into account the distribution of the electrons as given by the Schrodinger (wave) equation. It may be remarked that, since the two electrons are equivalent to one another,

$$H_{II I} = H_{II II}. \quad (15.7)$$

The matrix components of unity, viz., $\Delta_{II I}$ and $\Delta_{II II}$, which in this case are also the *normalization integrals*, are defined by

$$\Delta_{II I} = \int \int \psi_I \psi_I d\tau_1 d\tau_2 \quad \text{and} \quad \Delta_{II II} = \int \int \psi_{II} \psi_{II} d\tau_1 d\tau_2. \quad (15.8)$$

Since the 1s eigenfunctions as given in Table IV are already normalized, both integrals in equation (15.8) are equal to unity; further, since $\Delta_{II I}$ and $\Delta_{II II}$ are equal, because of the equivalence of the electrons, it follows that

$$\Delta_{II I} = \Delta_{II II} = 1. \quad (15.9)$$

The integrals $H_{II II}$ and $H_{II I}$ are also equal, and they are defined by

$$H_{II II} = H_{II I} = \int \int \psi_I \mathbf{H} \psi_{II} d\tau_1 d\tau_2. \quad (15.10)$$

These are called the *exchange integrals*, for they owe their existence to the possibility of two eigenfunctions, corresponding to the same energy state of the hydrogen molecule, arising from the interchange of the electrons between the two nuclei.

Finally, the *orthogonality integrals*, for which the symbol S^2 is often used, are represented by

$$\Delta_{II II} = \Delta_{II I} = \int \int \psi_I \psi_{II} d\tau_1 d\tau_2 \quad (15.11)$$

$$= S^2. \quad (15.12)$$

15b. Symmetric and Antisymmetric Solutions.—Making use of the values of the normalization and orthogonality integrals, and of the equality of the various matrix components, the secular equation (15.4) reduces to

$$\begin{vmatrix} H_{II I} - E & H_{II II} - S^2 E \\ H_{II II} - S^2 E & H_{II I} - E \end{vmatrix} = 0. \quad (15.13)$$

The solutions are

$$E_S = \frac{H_{II} + H_{III}}{1 + S^2} \quad (15.14)$$

and

$$E_A = \frac{H_{II} - H_{III}}{1 - S^2}, \quad (15.15)$$

the subscripts S and A referring to *symmetric* and *antisymmetric*, respectively, for reasons that will be made clear shortly.

It is now possible to determine the values of the coefficients a_1 and a_2 in the variation function, equation (15.3), utilizing the procedure described in the discussion of the variation treatment. The appropriate equation, of the form of (14.26), to be solved in this case is

$$a_1(H_{II} - \Delta_{II}E) + a_2(H_{III} - \Delta_{III}E) = 0. \quad (15.16)$$

Replacing Δ_{II} by unity, and Δ_{III} by S^2 , and inserting the value of E_S derived above, it is found that

$$a_1 = a_2, \quad (15.17)$$

and hence the symmetric eigenfunction corresponding to the energy E_S is given by

$$\psi_S = c_S(\psi_I + \psi_{II}) \quad (15.18)$$

where c_S represents the appropriate normalization factor. On the other hand, the antisymmetric eigenfunction, corresponding to the energy E_A , may be found by inserting the value given by equation (15.15) into equation (15.16); the result is

$$a_1 = -a_2 \quad (15.19)$$

and hence, by equation (15.3),

$$\psi_A = c_A(\psi_I - \psi_{II}) \quad (15.20)$$

where the normalization factor is now indicated by c_A .

In order to evaluate c_S and c_A , use is made of the normalizing conditions; thus, since ψ_S and ψ_A are real, and supposed to be normalized,

$$\int \int \psi_S \psi_S d\tau_1 d\tau_2 = 1 \quad \text{and} \quad \int \int \psi_A \psi_A d\tau_1 d\tau_2 = 1. \quad (15.21)$$

Inserting the expression for ψ_S , equation (15.18), it is seen that

$$\begin{aligned} \int \int \psi_S \psi_S d\tau_1 d\tau_2 &= c_S^2 \int \int (\psi_I + \psi_{II})^2 d\tau_1 d\tau_2 \\ &= c_S^2 \left(\int \int \psi_I^2 d\tau_1 d\tau_2 + \int \int \psi_{II}^2 d\tau_1 d\tau_2 + 2 \int \int \psi_I \psi_{II} d\tau_1 d\tau_2 \right). \end{aligned} \quad (15.22)$$

Since ψ_I and ψ_{II} are already normalized, and the orthogonality integral is

represented by S^2 , it follows, from equations (15.21) and (15.22), that

$$c_S^2(2 + 2S^2) = 1, \\ \therefore c_S = \frac{1}{\sqrt{2 + 2S^2}}. \quad (15.23)$$

Similarly, the value of c_A may be derived in an analogous manner from the normalization integral for ψ_A and the definition of the latter by equation (15.20); the result is

$$c_A = \frac{1}{\sqrt{2 - 2S^2}}. \quad (15.24)$$

Upon inserting the values for c_S and c_A into equations (15.18) and (15.20), respectively, the following results are obtained for the normalized eigenfunctions; the expressions for ψ_I and ψ_{II} are derived from equations (15.1) and (15.2).

$$\psi_S = \frac{1}{\sqrt{2 + 2S^2}} (\psi_I + \psi_{II}) \quad (15.25)$$

$$= \frac{1}{\sqrt{2 + 2S^2}} \{u_A(1)u_B(2) + u_A(2)u_B(1)\}, \quad (15.26)$$

and

$$\psi_A = \frac{1}{\sqrt{2 - 2S^2}} (\psi_I - \psi_{II}) \quad (15.27)$$

$$= \frac{1}{\sqrt{2 - 2S^2}} \{u_A(1)u_B(2) - u_A(2)u_B(1)\}. \quad (15.28)$$

It will be observed that if in ψ_S the coordinates of either the nuclei or the electrons are interchanged, i.e., A and B are exchanged or (1) and (2) are exchanged, the value of the eigenfunction remains unaltered. This eigenfunction is consequently said to be *symmetric* in the positional coordinates of both electrons and nuclei. On the other hand, if either of these pairs of coordinates in ψ_A are interchanged, the value of the eigenfunction as a whole changes its sign, and so it is referred to as *antisymmetric*. This accounts for the use of the subscripts S and A in equations (15.14) and (15.15), since E_S is the eigenvalue of the energy corresponding to the symmetric eigenfunction for the hydrogen molecule, while E_A corresponds to the antisymmetric eigenfunction.

15c. Evaluation of Coulombic Integral.—With the object of determining the actual energy eigenvalues E_S and E_A , it is now necessary to turn to the evaluation of the integrals H_{II} , H_{III} and S^2 . The Hamiltonian operator for the system of two electrons and two fixed nuclei may be written as

$$\mathbf{H} = -\frac{\hbar^2}{8\pi^2m} (\nabla_1^2 + \nabla_2^2) - (V_A + V_B) + V_{ab}. \quad (15.29)$$

where m is the mass of an electron, and ∇_1^2 and ∇_2^2 are the Laplacian operators with respect to the coordinates of electrons (1) and (2), respectively. For convenience, the potential energy V has been split up into three parts, V_A , V_B and V_0 . The quantities V_A and V_B represent the potential energies for interaction of the two electrons with the nuclei A and B, respectively, i.e.,

$$V_A = \frac{\epsilon^2}{r_{A1}} + \frac{\epsilon^2}{r_{A2}} \quad (15.30)$$

and

$$V_B = \frac{\epsilon^2}{r_{B1}} + \frac{\epsilon^2}{r_{B2}}, \quad (15.31)$$

whereas V_0 refers to the repulsion between the two nuclei and between the two electrons, i.e.,

$$V_0 = \frac{\epsilon^2}{r_{AB}} + \frac{\epsilon^2}{r_{12}}. \quad (15.32)$$

In these expressions ϵ is the unit electric charge, which is the same for the electrons and the hydrogen nuclei. The various distances are as indicated in Fig. 8.

It can be seen from equations (15.1), (15.5) and (15.29) that for the hydrogen molecule

$$\begin{aligned} H_{II} &= \int \int \psi_I \mathbf{H} \psi_I d\tau_1 d\tau_2 \\ &= \int \int u_A(1) u_B(2) \left\{ -\frac{h^2}{8\pi^2 m} (\nabla_1^2 + \nabla_2^2) - (V_A + V_B) + V_0 \right\} \\ &\quad \times u_A(1) u_B(2) d\tau_1 d\tau_2. \end{aligned} \quad (15.33)$$

Consider, now, the two separate hydrogen atoms, and suppose electron (1) to be associated with nucleus A, and electron (2) with nucleus B. The wave equation for the atom, which may be designated A(1), is then

$$\mathbf{H} u_A(1) = E_0 u_A(1), \quad (15.34)$$

or

$$\left\{ -\frac{h^2}{8\pi^2 m} (\nabla_1^2 + V_1) \right\} u_A(1) = E_0 u_A(1), \quad (15.35)$$

where V_1 is equal to ϵ^2/r_{A1} . Similarly, for atom B(2), the wave equation is

$$\left\{ -\frac{h^2}{8\pi^2 m} (\nabla_2^2 + V_2) \right\} u_B(2) = E_0 u_B(2), \quad (15.36)$$

where V_2 is ϵ^2/r_{B2} . In each case E_0 represents the energy of an isolated hydrogen atom in its normal state. It can be readily shown that by substituting equations (15.35) and (15.36) in equation (15.33), and then making use of the definitions of V_A , V_B and V_0 given by equations (15.30), (15.31)

and (15.32), respectively, the result is

$$H_{II} = \int \int u_A(1) u_B(2) \left(2E_0 + \frac{\epsilon^2}{r_{AB}} + \frac{\epsilon^2}{r_{12}} - \frac{\epsilon^2}{r_{A2}} - \frac{\epsilon^2}{r_{B1}} \right) u_A(1) u_B(2) d\tau_1 d\tau_2. \quad (15.37)$$

Because the eigenfunctions $u_A(1)$ and $u_B(2)$ are normalized, and since the expression for the interaction between the electrons, $u_A(1)u_B(2)$, is independent of E_0 and of r_{AB} , the nuclei being fixed, but not of r_{12} , r_{A2} or r_{B1} , the expression (15.37) for H_{II} can be rewritten as

$$H_{II} = 2E_0 + \frac{\epsilon^2}{r_{AB}} + \epsilon^2 \int \int \frac{1}{r_{12}} \{u_A(1)u_B(2)\}^2 d\tau_1 d\tau_2 - \epsilon^2 \int \int \left(\frac{1}{r_{A2}} + \frac{1}{r_{B1}} \right) \{u_A(1)u_B(2)\}^2 d\tau_1 d\tau_2. \quad (15.38)$$

For convenience this equation for the coulombic integral may be put in the form

$$H_{II} = 2E_0 + \frac{\epsilon^2}{r_{AB}} + J_1 - 2J_2, \quad (15.39)$$

where J_1 and J_2 are defined as follows,

$$J_1 = \epsilon^2 \int \int \frac{1}{r_{12}} \{u_A(1)u_B(2)\}^2 d\tau_1 d\tau_2, \quad (15.40)$$

and, since the two electrons are equivalent,

$$J_2 = \epsilon^2 \int \int \frac{1}{r_{A2}} \{u_A(1)u_B(2)\}^2 d\tau_1 d\tau_2 \quad (15.41)$$

$$= \epsilon^2 \int \int \frac{1}{r_{B1}} \{u_A(1)u_B(2)\}^2 d\tau_1 d\tau_2. \quad (15.42)$$

The evaluation of these integrals is by no means simple, but the type of procedure that may be adopted is indicated by the treatment given below. Consider first the electronic configurations implied by $u_A(1)$ and $u_B(2)$; these are $1s$ wave functions of the normal hydrogen atom, and hence from the expression for ψ_{100} in Table IV (p. 58), with $Z = 1$, it follows that

$$u_A(1) = \frac{1}{\sqrt{\pi a_0^3}} e^{-r_{A1}/a_0} \quad (15.43)$$

and

$$u_B(2) = \frac{1}{\sqrt{\pi a_0^3}} e^{-r_{B2}/a_0}. \quad (15.44)$$

Instead of using the distances r_{A1} and r_{B2} , it is more convenient to express these quantities in terms of the so-called *atomic units*, that is, in terms of the

first Bohr orbit of the normal hydrogen atom (a_0), so that

$$u_A(1) = \frac{1}{\sqrt{\pi a_0^3}} e^{-\rho_{A1}} \quad \text{and} \quad u_B(2) = \frac{1}{\sqrt{\pi a_0^3}} e^{-\rho_{B2}}, \quad (15.45)$$

where ρ_{A1} is equal to r_{A1}/a_0 , and ρ_{B2} is r_{B2}/a_0 .

In the integral J_1 the term ϵ^2/r_{12} is the classical value of the repulsive force between the two electrons, while the term involving the integral of $\{u_A(1)u_B(2)\}^2 d\tau_1 d\tau_2$ gives the electronic distribution on the basis of the wave mechanics. It is apparent, therefore, that J_1 is equal to the repulsive energy between the two electronic charge distributions, the latter being determined by the respective electron (orbital) eigenfunctions. The same energy quantity may be arrived at by multiplying the total charge distribution of electron (1) associated with nucleus A, by the potential distribution resulting from electron (2) about the nucleus B. The actual value of the charge distribution of electron (1) is given by the integral of $\{u_A(1)\}^2 d\tau_1$ over the configuration space of this electron, multiplied by the unit electronic charge ϵ . If the value of the eigenfunction $u_A(1)$ from equation (15.45) is utilized, it is seen that this charge distribution is equal to

$$\begin{aligned} \epsilon \int \{u_A(1)\}^2 d\tau_1 &= \epsilon \int \left(\frac{1}{\sqrt{\pi a_0^3}} e^{-\rho_{A1}} \right)^2 d\tau_1 \\ &= \frac{\epsilon}{\pi} \int e^{-2\rho_{A1}} d\tau_1, \end{aligned} \quad (15.46)$$

where the volume element $d\tau_1$ in the last expression is equal to $d\tau_1/a_0^3$ of the preceding integral, and hence is in atomic units.

Making use of a similar expression for the charge distribution about the nucleus B, it can be shown by electrostatic theory that the corresponding potential function is given by

$$V(\rho_{B1}) = \frac{\epsilon}{a_0 \rho_{B1}} \{1 - e^{-2\rho_{B1}}(1 + \rho_{B1})\}, \quad (15.47)$$

where ρ_{B1} is equivalent to r_{B1}/a_0 . The integral J_1 may thus be equated to the product of equations (15.46) and (15.47), i.e.,

$$\begin{aligned} J_1 &= V(\rho_{B1}) \frac{\epsilon}{\pi} \int e^{-2\rho_{A1}} d\tau_1 \\ &= \frac{\epsilon^2}{a_0 \pi} \int \frac{1}{\rho_{B1}} e^{-2\rho_{A1}} \{1 - e^{-2\rho_{B1}}(1 + \rho_{B1})\} d\tau_1. \end{aligned} \quad (15.48)$$

In the evaluation of the various integrals involved in the hydrogen molecule problem, it is convenient to utilize *confocal elliptic coordinates*; two of these, λ and μ , are given by the relationships

$$\lambda = \frac{1}{D} (\rho_{A1} + \rho_{B1}) \quad \text{and} \quad \mu = \frac{1}{D} (\rho_{A1} - \rho_{B1}), \quad (15.49)$$

and, consequently,

$$\rho_{A1} = \frac{1}{2}D(\lambda + \mu) \quad \text{and} \quad \rho_{B1} = \frac{1}{2}D(\lambda - \mu), \quad (15.50)$$

where D is equal to r_{AB} in atomic units, i.e., to r_{AB}/a_0 . The third coordinate is θ , the angle between a fixed plane through the nuclei and the plane passing through the nuclei and the electron. In terms of the new coordinates the volume element $d\tau_1$, i.e., $dx_1dy_1dz_1$, may be represented by

$$d\tau_1 = \frac{1}{8}D^3(\lambda^2 - \mu^2)d\lambda d\mu d\theta, \quad (15.51)$$

omitting the subscripts for simplicity. Hence equation (15.48) becomes

$$J_1 = \frac{\epsilon^2}{a_0\pi} \cdot \frac{D^2}{4} \iiint \frac{e^{-D(\lambda-\mu)}}{\lambda - \mu} \times \left[1 - e^{-D(\lambda-\mu)} \left\{ 1 + \frac{D}{2}(\lambda - \mu) \right\} \right] (\lambda^2 - \mu^2) d\lambda d\mu d\theta. \quad (15.52)$$

In order to integrate over the whole of the configuration space of electron (1), the limits are readily seen to be as follows: from 0 to 2π for θ , from 1 to ∞ for λ , and from -1 to $+1$ for μ . Integration by standard methods then leads to the result

$$J_1 = \frac{\epsilon^2}{a_0} \left\{ \frac{1}{D} - e^{-2D} \left(\frac{1}{D} + \frac{11}{8} + \frac{3}{4}D + \frac{1}{6}D^2 \right) \right\}. \quad (15.53)$$

By means of arguments similar to those used in the evaluation of J_1 , it is seen that J_2 may be regarded as the attractive energy resulting from the interaction of the electronic charge distribution about one of the nuclei with the positive charge of the other nucleus. This is equal to the product of the nuclear charge ϵ and the potential function at that nucleus due to the charge of the electron associated with the other nucleus. The latter quantity is given by an expression analogous to (15.47), viz.,

$$V(D) = \frac{\epsilon}{a_0D} \{ 1 - e^{-2D}(1 + D) \}, \quad (15.54)$$

where, as before, D is equal to r_{AB}/a_0 . It follows, therefore, that

$$\begin{aligned} J_2 &= \epsilon V(D) \\ &= \frac{\epsilon^2}{a_0D} \{ 1 - e^{-2D}(1 + D) \}. \end{aligned} \quad (15.55)$$

Combination of the expressions for J_1 and J_2 with equation (15.39) then gives for the coulombic integral

$$H_{II} = H_{IIII} = 2E_0 + \frac{\epsilon^2}{a_0} e^{-2D} \left(\frac{1}{D} + \frac{5}{8} - \frac{3}{4}D - \frac{1}{6}D^2 \right). \quad (15.56)$$

15d. Evaluation of Exchange Integral.—Attention must now be directed to the determination of the exchange integral, H_{II} ; inserting the expression (15.29) for the Hamiltonian operator, this becomes

$$\begin{aligned} H_{II} &= \int \int \psi_I \mathbf{H} \psi_{II} d\tau_1 d\tau_2 \\ &= \int \int u_A(1) u_B(2) \left\{ -\frac{\hbar^2}{8\pi^2 m} (\nabla_1^2 + \nabla_2^2) - (V_A + V_B) + V_0 \right\} \\ &\quad \times u_A(2) u_B(1) d\tau_1 d\tau_2. \end{aligned} \quad (15.57)$$

Making use of the wave equations for the separated hydrogen atoms A(2) and B(1), that is,

$$\left\{ -\frac{\hbar^2}{8\pi^2 m} (\nabla_1^2 + V_1) \right\} u_B(1) = E_0 u_B(1) \quad (15.58)$$

and

$$\left\{ -\frac{\hbar^2}{8\pi^2 m} (\nabla_2^2 + V_2) \right\} u_A(2) = E_0 u_A(2), \quad (15.59)$$

where V_1 is equal to ϵ^2/r_{B1} and V_2 is ϵ^2/r_{A2} , then equation (15.57) reduces to

$$H_{II} = \int \int u_A(1) u_B(2) \left(2E_0 + \frac{\epsilon^2}{r_{AB}} + \frac{\epsilon^2}{r_{12}} - \frac{\epsilon^2}{r_{A1}} - \frac{\epsilon^2}{r_{B2}} \right) u_A(2) u_B(1) d\tau_1 d\tau_2 \quad (15.60)$$

$$= 2E_0 S^2 + \frac{\epsilon^2}{r_{AB}} S^2 + K_1 - 2K_2. \quad (15.61)$$

In equation (15.61), S^2 is the orthogonality integral, as before, and

$$K_1 = \epsilon^2 \int \int \frac{1}{r_{12}} \{ u_A(1) u_B(2) u_A(2) u_B(1) \} d\tau_1 d\tau_2 \quad (15.62)$$

and K_2 is given either by the equation

$$K_2 = \epsilon^2 \int \int \frac{1}{r_{A1}} \{ u_A(1) u_B(2) u_A(2) u_B(1) \} d\tau_1 d\tau_2, \quad (15.63)$$

or by an exactly similar, and equivalent, equation in which $1/r_{B2}$ replaces $1/r_{A1}$. The expression for K_2 may be separated into two parts, each involving functions of one electron only; thus,

$$\begin{aligned} K_2 &= \epsilon^2 \int \frac{1}{r_{A1}} \{ u_A(1) u_B(1) \} d\tau_1 \int u_A(2) u_B(2) d\tau_2 \\ &= KS, \end{aligned} \quad (15.64)$$

where

$$K = \epsilon^2 \int \frac{1}{r_{A1}} \{u_A(1)u_B(1)\} d\tau_1 \quad (15.65)$$

and

$$S = \int u_A(2)u_B(2) d\tau_2. \quad (15.66)$$

It should be noted that this quantity S is identical with that involved in the S^2 used to represent the orthogonality integral, as may be shown in the following manner. By definition,

$$\begin{aligned} S^2 &= \int \int \psi_I \psi_{II} d\tau_1 d\tau_2 \\ &= \int \int u_A(1)u_B(2)u_A(2)u_B(1) d\tau_1 d\tau_2. \end{aligned} \quad (15.67)$$

Separating the terms referring to the electrons (1) and (2), this becomes

$$S^2 = \int u_A(1)u_B(1) d\tau_1 \int u_A(2)u_B(2) d\tau_2. \quad (15.68)$$

Since the two electrons are equivalent, it is apparent that the two integrals in equation (15.68) must be identical; hence each may be put equal to S , as defined by equation (15.66).

Returning to equation (15.65), upon insertion of the appropriate hydrogen atom $1s$ eigenfunctions for $u_A(1)$ and $u_B(1)$ this becomes

$$K = \frac{\epsilon^2}{\pi a_0^3} \int \frac{1}{r_{A1}} e^{-(r_{A1}+r_{B1})/a_0} d\tau_1 \quad (15.69)$$

$$= \frac{\epsilon^2}{\pi a_0} \int \frac{1}{\rho_{A1}} e^{-(\rho_{A1}+\rho_{B1})} d\tau_1, \quad (15.70)$$

the distances being now expressed in terms of atomic units, i.e., $r_{A1}/a_0 = \rho_{A1}$ and $r_{B1}/a_0 = \rho_{B1}$. In equation (15.70) the volume element $d\tau_1$, is equal to $d\tau_1/a_0^3$ of the previous equation (15.69), and hence it is also in atomic units. As before, transformation to confocal elliptic coordinates gives

$$K = \frac{\epsilon^2}{\pi a_0} \cdot \frac{D^2}{4} \int \int \int e^{-D\lambda(\lambda - \mu)} d\lambda d\mu d\theta, \quad (15.71)$$

and upon integration between the limits mentioned in connection with the evaluation of J_1 , it is found that

$$K = \frac{\epsilon^2}{a_0} e^{-D}(1 + D). \quad (15.72)$$

A similar treatment applied to equation (15.66) for S yields

$$\begin{aligned} S &= \int u_A(2)u_B(2)d\tau_2 \\ &= \frac{1}{\pi a_0^3} \int e^{-(r_{A2}+r_{B2})/a_0} d\tau_2 \\ &= \frac{1}{\pi} \int e^{-(\rho_{A2}+\rho_{B2})} d\tau_2. \end{aligned} \quad (15.73)$$

After transforming to elliptic coordinates, it is seen that

$$S = \frac{D^3}{8\pi} \int \int \int e^{-D\lambda(\lambda^2 - \mu^2)} d\lambda d\mu d\theta,$$

and integration between the same limits as before, for the whole of the configuration space, gives

$$S = e^{-D}(1 + D + \frac{1}{3}D^2). \quad (15.74)$$

The value of the orthogonality integral S^2 , which is required for the solution of the hydrogen molecule problem, is thus

$$S^2 = e^{-2D}(1 + D + \frac{1}{3}D^2)^2. \quad (15.75)$$

Further, by combining the expressions, equations (15.70) and (15.74), for K and S , respectively, it is found that (cf. equation (15.64)),

$$K_2 = KS = \frac{\epsilon^2}{a_0} e^{-2D}(1 + 2D + \frac{4}{3}D^2 + \frac{1}{3}D^3). \quad (15.76)$$

The final integral to be evaluated is K_1 , as given by equation (15.62); this is exceptionally difficult, but Sugiura⁴ derived the result

$$\begin{aligned} K_1 &= \frac{\epsilon^2}{5a_0} \left[e^{-2D} \left(\frac{25}{8} - \frac{23}{4}D - 3D^2 - \frac{1}{3}D^3 \right) \right. \\ &\quad \left. + \frac{6}{D} \{ S^2(C + \ln D) + S_1^2 E_i(-4D) - 2SS_1 E_i(-2D) \} \right], \end{aligned} \quad (15.77)$$

where C is Euler's constant, defined by

$$C = \int_0^\infty \left(\frac{1}{1+x^2} - \frac{1}{e^x} \right) \frac{dx}{x} = 0.5772 \dots,$$

$$S_1 = e^D(1 - D + \frac{1}{3}D^2),$$

⁴ Sugiura, *Z. Physik*, **45**, 484 (1927).

and E_i represents the function known as the *exponential integral*, defined by

$$E_i(-x) = \int_x^\infty \frac{1}{u} e^{-u} du.$$

Values of this integral for various values of x are to be found in tables of mathematical functions. If x is not too large, it is possible to write

$$E_i(-x) = C + \ln|x| - x + \frac{1}{2} \cdot \frac{x^2}{2!} - \frac{1}{3} \cdot \frac{x^3}{3!} + \dots$$

where, as before, C is Euler's constant.

15e. Energy of the Molecular Hydrogen System.—By combining equations (15.39) and (15.61) for H_{II} and H_{III} , respectively, and equations (15.14) and (15.15) for E_S and E_A , it is seen that

$$E_S - 2E_0 = \frac{\epsilon^2}{r_{AB}} + \frac{J_1 - 2J_2 + K_1 - 2K_2}{1 + S^2} \quad (15.78)$$

and

$$E_A - 2E_0 = \frac{\epsilon^2}{r_{AB}} + \frac{J_1 - 2J_2 - K_1 + 2K_2}{1 - S^2}. \quad (15.79)$$

In each case, $E - 2E_0$ represents the difference between the energy of the molecular hydrogen system and that of two separated normal hydrogen atoms. It is, in other words, the interaction energy of the two atoms as they are brought closer together. This quantity is generally referred to as the potential energy of the system, the energy of the atoms being taken as zero. In the equations given above, the integrals J_1 , J_2 , K_1 , K_2 and S have been expressed as functions of D , and consequently of the internuclear distance r_{AB} , since D is equal to r_{AB}/a_0 . It is thus possible to evaluate the potential energy for the molecular hydrogen system for various distances of separation of the two atoms. There will evidently be two distinct sets of results, one for E_S and one for E_A , corresponding to the symmetric and antisymmetric eigenfunctions, respectively, of the system. The results obtained in this manner by Sugiura, with energies expressed in kcal. per mole, are plotted against the corresponding internuclear distances in Fig. 9.

An examination of the two curves reveals the fact that only in the case of the symmetric (orbital) eigenfunction, for which the energy is E_S , is a stable hydrogen molecule possible. The values of the potential energy E_A for the antisymmetric state are seen to be positive for all internuclear distances; this means that the two hydrogen atoms will always repel each other, the extent of repulsion increasing as the nuclei are brought closer together. However, in spite of the fact that the antisymmetric electron eigenfunction does not lead to a stable molecule, there is evidence that an unstable $^3\Sigma_u^+$ state, which would correspond to this molecule, is involved in certain continuous spectra. On the other hand, for the state corresponding to the symmetric orbital, the interaction (potential) energy becomes, at first, in-

creasingly negative as the two nuclei approach; this means that there is an increasing attraction between the two hydrogen atoms. The attraction continues to increase until the minimum point M in Fig. 9 is reached; beyond this point there is at first a gradual and then a more rapid decrease in the net attractive force, leading eventually to a resultant repulsion, indicated by the interaction energy becoming positive at small internuclear distances. The minimum M of the potential energy curve thus represents the equilibrium state of the hydrogen molecule, and the curve marked E_s indicates the variation of potential energy with internuclear distance in the normal, or stable, hydrogen molecule.

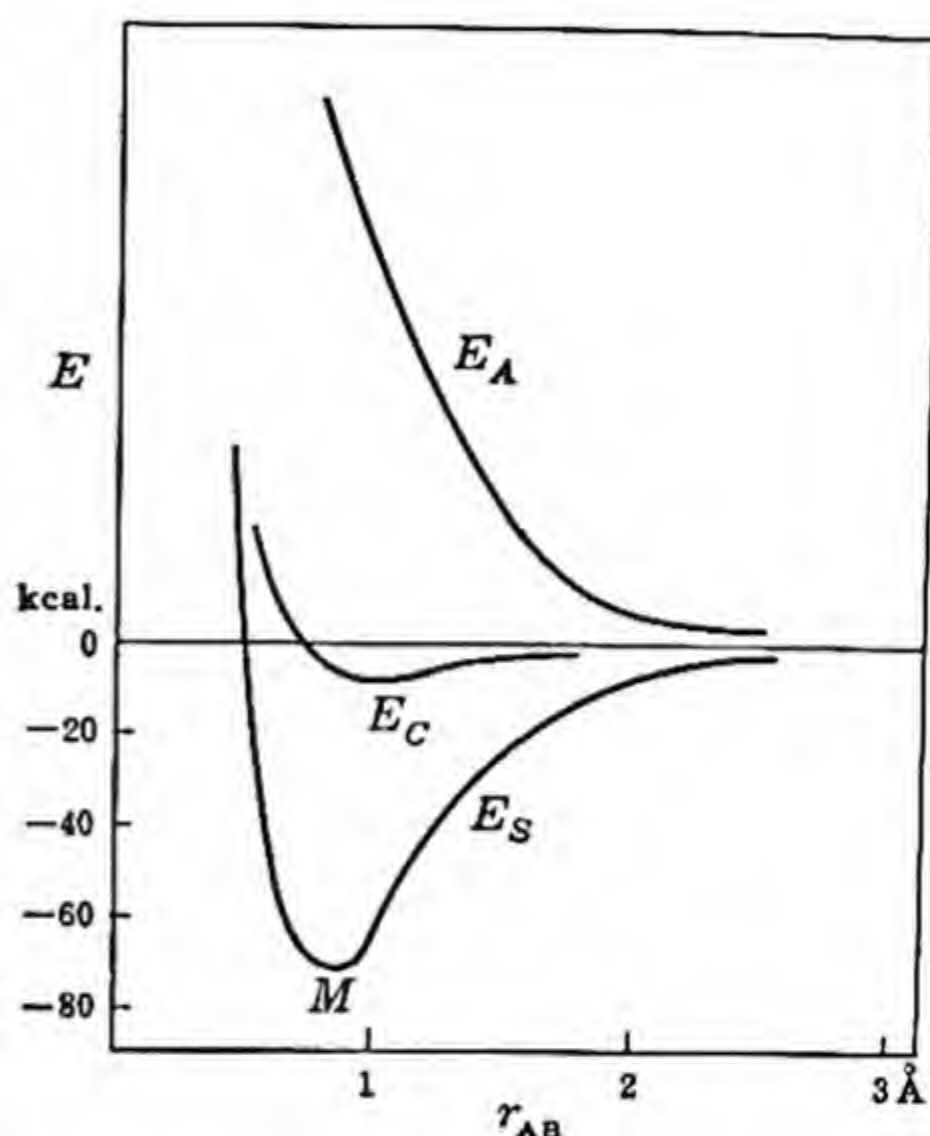


FIG. 9. Potential energy of hydrogen molecule

According to the results in Fig. 9, the equilibrium distance between the hydrogen nuclei in the normal molecule, that is, the value of r_{AB} at the minimum M , is 0.80 \AA , while the corresponding potential energy, which is numerically equal to the heat of dissociation of the normal molecule at 0° K , plus the zero-point energy, is about $-72 \text{ kcal. per mole}$. The corresponding experimental values, obtained from a study of the band spectra of molecular hydrogen (cf. Chapter IV), are 0.74 \AA and $-108.9 \text{ kcal. per mole}$, respectively. Although the results derived theoretically by means of quantum mechanics are of the correct order of magnitude, they are seen to be somewhat in error. The origin of these discrepancies lies in the choice of a too simple variation function; it will be seen later that by improving the eigenfunction for the molecular hydrogen system it is possible to calculate the internuclear distance and potential energy (heat of dissociation) in the equilibrium state in almost exact agreement with experiment.

REFINED TREATMENT OF HYDROGEN MOLECULE

16a. Use of Atomic Orbitals.—Several attempts have been made to refine the wave mechanical treatment of the hydrogen molecule by improving the trial eigenfunctions used in the variation procedure. Some of these have been based on the wave functions for separated hydrogen atoms, i.e., *atomic orbitals*, such as were employed by Heitler and London, while others have used eigenfunctions of a different type to be discussed below. In the treat-

ment adopted by Wang,⁵ the $1s$ atomic orbitals, $u_A(1)$, $u_B(1)$, etc. as given by equations (15.43) and (15.44), were modified by the introduction of an effective nuclear charge Z' in place of Z equal to unity; the resulting eigenfunctions were thus of the form $Ce^{-Z'r/a_0}$, where C is a normalization constant. The value of Z' necessary to minimize the energy in the equilibrium state was found to be 1.166, the corresponding internuclear distance being 0.76 Å, and the heat of dissociation, equal to the potential energy but of opposite sign, 86.6 kcal. per mole. A simple modification in the eigenfunction thus leads to a considerable improvement in the calculated dimensions and binding energy of the hydrogen molecule.

A further development of Wang's treatment was made by Rosen,⁶ who introduced additional terms to allow for the mutual polarization of the hydrogen atoms, that is, for the distortion of the charge distribution of one atom as it is brought closer to the other. The modified $u_A(1)$ atomic orbital used by Wang was multiplied by a factor of the form $1 + \sigma r_{A1} \cos \theta_{A1}$, where σ is a variable parameter and θ_{A1} is the angle between r_{A1} and the line joining the nuclei (cf. Fig. 8). The other eigenfunctions were modified in an analogous manner. It can be seen that when the angle θ is small, that is, when the electron is in the region between the nuclei, the eigenfunction is increased over the normal $1s$ value; in other words, the effect of the correction is to make the electron (cloud) distribution of each atom bulge out in the direction of the other atom. That this is due to the factor $1 + \sigma r \cos \theta$ may be seen in another manner: multiplying by the Wang $1s$ orbital, the correction term is seen to take the form $C'e^{-Z'r/a_0} \cos \theta$, and an examination of the hydrogen-like eigenfunctions in Table IV shows that this has the characteristic of a $2p$ orbital. As already observed, such eigenfunctions are not spherically symmetrical, but have larger values in certain directions. This is just what would be expected from the mutual polarization of the two atoms in the hydrogen molecule. By first taking σ as zero, Rosen obtained a best value of 1.19 for the effective charge Z' , and then with σ equal to 0.10 for the equilibrium state, the internuclear distance was calculated to be 0.77 Å and the binding energy 92.6 kcal. per mole.

16b. Molecular Orbital Methods.—In the foregoing treatments of the hydrogen molecule the eigenfunction for the molecular system has been derived by combining atomic orbitals, i.e., orbital eigenfunctions for an electron in the field of a single nucleus. An alternative approach, based on the proposals of Hund, Mulliken, and others,⁷ makes use of what are known as *molecular orbitals*. These are wave functions in which an attempt is made to take into account the behavior of each electron in the field of all the other electrons and nuclei of the molecule. If ψ_1 , ψ_2 , etc., are the molecular orbitals of the individual electrons, then it is supposed that the eigenfunction

⁵ Wang, *Phys. Rev.*, **31**, 579 (1928).

⁶ Rosen, *Phys. Rev.*, **38**, 2099 (1931).

⁷ Hund, *Z. Physik*, **73**, 1 (1931); Mulliken, *J. Chem. Phys.*, **1**, 492 (1933); **3**, 375 (1935); *Chem. Rev.*, **9**, 347 (1931); Hückel, *Z. Physik*, **60**, 423 (1930); **72**, 310 (1931), etc.; see also, Lennard-Jones, *Trans. Faraday Soc.*, **25**, 668 (1929).

for the system as a whole, containing n electrons, is given by

$$\psi_{\text{M.O.}} = \psi_1 \psi_2 \psi_3 \cdots \psi_n, \quad (16.1)$$

where the subscript M.O. is used to indicate that molecular orbitals are being employed.

As a convenient approximation each of the molecular orbitals, $\psi_1, \psi_2, \cdots, \psi_n$, is expressed as a linear combination of atomic orbitals; this does not necessarily give the best molecular orbital, but it does give a form which is reasonably adequate in many cases. In the molecular hydrogen system there are two electrons, and the atomic orbitals will be the same as the normal $1s$ orbitals, viz., $u_A(1), u_B(1), u_A(2)$ and $u_B(2)$, employed in the Heitler-London treatment. The molecular orbital ψ_1 , for the electron (1) in the field of the two nuclei A and B, may then be taken as the linear combination $\{u_A(1) + u_B(1)\}$, the coefficients being the same since the two nuclei are equivalent. Similarly, the molecular orbital ψ_2 for the electron (2) will then be $\{u_A(2) + u_B(2)\}$. Making use of equation (16.1), it is then seen that the orbital eigenfunction for the system of two electrons in the field of the two nuclei, as in the hydrogen molecule, would be

$$\psi_{\text{M.O.}} = \psi_1 \psi_2 = \{u_A(1) + u_B(1)\} \{u_A(2) + u_B(2)\} \quad (16.2)$$

$$= u_A(1)u_A(2) + u_B(1)u_B(2) + u_A(1)u_B(2) + u_A(2)u_B(1), \quad (16.3)$$

apart from the normalization factor. The last two terms of equation (16.3) are identical with the Heitler-London symmetric eigenfunction, equation (15.26); the first two terms, however, represent a type of structure not yet considered. It will be observed that the first term, $u_A(1)u_A(2)$, implies that both electrons (1) and (2) are associated with the nucleus A; this means an ionic structure of the type $H_A^- H_B^+$. On the other hand, in the second term, $u_B(1)u_B(2)$, both electrons are on nucleus B, which means the ionic structure $H_A^+ H_B^-$.

16c. Ionic Terms.—The effect of the molecular orbital procedure outlined above is thus to introduce *ionic terms* in addition to the *homopolar terms* of the Heitler-London treatment. It will be observed that the two ionic terms, corresponding to the structures $H^- H^+$ and $H^+ H^-$, appear with the same coefficient in the eigenfunction for the system. This is to be expected, since the hydrogen molecule has no resultant dipole moment. If the atoms A and B had been different, the molecular orbitals for the separate electrons would have been of the form $\{au_A(1) + bu_B(1)\}$ and $\{au_A(2) + bu_B(2)\}$, the coefficients a and b being generally different; the resultant eigenfunction would then be

$$\psi_{\text{M.O.}} = a^2 \{u_A(1)u_A(2)\} + b^2 \{u_B(1)u_B(2)\} + ab \{u_A(1)u_B(2) + u_A(2)u_B(1)\}. \quad (16.4)$$

If a is greater than b , then the form $A^- B^+$ would predominate over $A^+ B^-$, whereas if a were less than b , the reverse would be true. In either case,

the molecule would be polar, the direction of the dipole moment depending on the relative values of a and b which are determined by the relative electronegativities of the atoms A and B (cf. Section 21b).

There is little doubt that the Heitler-London (homopolar) treatment of the hydrogen molecule is incomplete, as it does not make allowance for ionic terms, that is, for the probability of both electrons being associated with either one or other of the two nuclei. On the other hand, the simple molecular orbital treatment, which leads to equation (16.3) for the orbital eigenfunction of the hydrogen molecule, attaches too much importance to the ionic terms, since they appear with the same coefficient (unity) as do the homopolar terms. The true state of affairs probably lies somewhere between these extremes, and an eigenfunction of the form

$$\psi_{\text{M.O.}} = \{u_A(1)u_A(2) + u_B(1)u_B(2)\} + C\{u_A(1)u_B(2) + u_A(2)u_B(1)\}, \quad (16.5)$$

in which the homopolar terms are included with a coefficient C , compared with unity for the ionic terms, was proposed by Weinbaum.⁸ Employing this as a variation function, with different values of C , and using an effective nuclear charge Z' in the $1s$ atomic orbitals, the minimum value for the binding energy 92.2 kcal. per mole was found for Z' equal to 1.193 and C to 3.9. The corresponding internuclear distance, for the equilibrium state of the normal hydrogen molecule, was calculated to be 0.77 Å. These results are almost as good as those obtained by Rosen, who used a more involved calculation. Since the coefficient C in equation (16.5) is 3.9, it appears that in the eigenfunction of normal hydrogen, the contribution of the homopolar terms is about four times as great as that of the ionic terms.

The method used by Weinbaum, described in the preceding paragraph, is equivalent to Wang's treatment with the addition of ionic terms; since this resulted in an improvement of 7.6 kcal. per mole in the calculated potential energy of the equilibrium state of molecular hydrogen, an attempt was made to apply the same correction to Rosen's calculations. This led to a value of 94.5 kcal. per mole for the dissociation energy of the hydrogen molecule, which is little better than that obtained by Rosen without making any allowance for ionic structures.

16d. Method of Coolidge and James.—A more complicated form of the molecular orbital procedure, which has given a value for the heat of dissociation of hydrogen in almost exact agreement with the best spectroscopic values, has been carried out by James and Coolidge.⁹ This calculation represents one of the remarkable achievements of quantum mechanics as applied to chemical problems. One reason why the simple molecular orbital method leads to too great a preponderance of ionic terms is because the eigenfunction does not take into account the mutual repulsion of the electrons, and the same defect exists in all treatments of the hydrogen molecule already described. It is true that the Hamiltonian (energy) operator in-

⁸ Weinbaum, *J. Chem. Phys.*, 1, 593 (1933).

⁹ James and Coolidge, *J. Chem. Phys.*, 1, 825 (1933); 3, 129 (1935).

cludes a term for the interaction of the electrons [cf. equation (15.32)], but an appropriate allowance should also be made in the eigenfunction for the system. In addition to the four parameters represented by the distances r_{A1} , r_{A2} , r_{B1} and r_{B2} in the molecular eigenfunction, James and Coolidge introduced a fifth parameter r_{12} , the distance between the two electrons, to allow for their mutual interaction. Defining the elliptic coordinates

$$\lambda_1 = \frac{r_{A1} + r_{B1}}{r_{AB}}, \quad \lambda_2 = \frac{r_{A2} + r_{B2}}{r_{AB}}$$

$$\mu_1 = \frac{r_{A1} - r_{B1}}{r_{AB}} \quad \text{and} \quad \mu_2 = \frac{r_{A2} - r_{B2}}{r_{AB}},$$

and the new parameter

$$\rho = \frac{2r_{12}}{r_{AB}},$$

the variation function of James and Coolidge is given by the series

$$\psi = \frac{1}{2\pi} e^{-\delta(\lambda_1 + \lambda_2)/a_0} \sum_{mnjkp} c_{mnjkp} (\lambda_1^m \lambda_2^n \mu_1^j \mu_2^k \rho^p + \lambda_1^n \lambda_2^m \mu_1^k \mu_2^j \rho^p), \quad (16.6)$$

where δ is a variable, approximately equal to $\frac{1}{2}r_{AB}$. It can be seen that if the orbitals which make up this molecular orbital were simple $1s$ hydrogen atom orbitals, δ would be exactly $\frac{1}{2}r_{AB}$.

The summation represented in equation (16.6) extends over positive, integral and zero values of the indices, m , n , j , k and p , subject to the restriction that $j + k$ must be even, for this is required by considerations of nuclear symmetry. As many terms are taken in the summation as are necessary to give an acceptable result for the energy of the hydrogen molecule. Calculations were first carried out with a limited number of terms in order to find a suitable value for the parameter δ . Assuming r_{AB} to be equal to the experimental internuclear distance $1.40a_0$, the minimum energy was found with δ equal to $0.75a_0$. These were subsequently shown to be the best values for r_{AB} and δ , when as many as eleven terms were included in the eigenfunction. The various coefficients c , for the different indices, were determined by the variation procedure, and then the energy was calculated by the integral $E = \int \psi H \psi d\tau$, assuming the ψ 's to be normalized (cf. Section 14c). Using only five terms in the summation, the binding energy of the hydrogen molecule was calculated to be 103.8 kcal., but eleven terms gave a value of 108.0 kcal. per mole. A further two terms led to a relatively small change, namely to 108.3 kcal. per mole. Since the improvement obtained by the addition of further terms did not justify the very arduous calculations, they were not extended beyond thirteen terms. From the rate of convergence, however, it was estimated that the limiting value for the energy at the minimum of the potential energy curve would be 108.9 kcal., with the interatomic distance as 0.74 Å. These results are, within the limits of experimental error, in exact agreement with those derived from the spectrum of molecular hydrogen.

It is of interest to record that if p in equation (16.6) is taken as zero, so that the r_{12} parameter, which takes into account in the eigenfunction the mutual repulsion of the electrons, is omitted, the calculated energy is 98.5 kcal. The tendency of the electron clouds in molecular hydrogen to avoid one another thus has a considerable effect on the energy. It is easy to understand, therefore, why the treatments of Rosen and of Weinbaum gave binding energies which could not be made to exceed about 95 kcal. per mole.

RESONANCE

17a. Coulombic Energy in the Hydrogen Molecule.—It was seen in connection with the Heitler-London treatment of the hydrogen molecule that because the interchange of the electrons (1) and (2) between the two nuclei A and B does not alter the energy, the molecular hydrogen system is doubly degenerate for large internuclear distances. That is to say, under these conditions there are two eigenfunctions, given by equations (15.1) and (15.2), corresponding to the same value of the energy. As the nuclei are brought closer together, the degeneracy is removed and two different states of the hydrogen molecule, corresponding to the symmetric and antisymmetric eigenfunctions, can exist, at least theoretically. Suppose, however, that the exchange of electrons were not possible; there would then be only one eigenfunction for the system, viz., $u_A(1)u_B(2)$, assuming electron (1) to be associated with the hydrogen nucleus A, and electron (2) with nucleus B. The secular equation for the energy, which will now have only one possible value, designated by E_C , would be

$$H_{II} - \Delta_{II}E_C = 0, \quad (17.1)$$

where

$$H_{II} = \int \int u_A(1)u_B(2) \mathbf{H} u_A(1)u_B(2) d\tau_1 d\tau_2 \quad (17.2)$$

and

$$\Delta_{II} = \int \int u_A(1)u_B(2)u_A(1)u_B(2) d\tau_1 d\tau_2. \quad (17.3)$$

Since the $1s$ eigenfunctions are supposed to be normalized, Δ_{II} is unity, and so by equation (17.1)

$$E_C = H_{II}. \quad (17.4)$$

The integral H_{II} appearing here is evidently identical with that considered previously, equation (15.33), since the Hamiltonian operator is the same in both cases; it follows, therefore, using equation (15.39), that

$$E_C = 2E_0 + \frac{e^2}{r_{AB}} + J_1 - 2J_2 \quad (17.5)$$

or

$$E_C - 2E_0 = \frac{e^2}{r_{AB}} + J_1 - 2J_2. \quad (17.6)$$

Utilizing the expressions for the integrals J_1 and J_2 , equations (15.53) and (15.55), it is possible to calculate the potential energy E_c , taking that of the separated atoms ($2E_0$) as zero, as before, for various values of the internuclear distance r_{AB} . The results obtained in this manner are plotted in Fig. 9, where they may be compared with those given by the symmetric and antisymmetric electron eigenfunctions. It is seen that the nature of the E_c curve indicates that there would never be any great attractive force between the hydrogen atoms; in fact, at the equilibrium separation of the atoms E_c is less than 20 per cent of the total binding energy holding the two atoms together in a molecule of hydrogen.

From the discussion in connection with the evaluation of the integrals involved in H_{II} , it will be apparent that $(e^2/r_{AB}) + J_1 - 2J_2$, which is equal to E_c , with E_0 taken as zero, represents the classical, or coulombic, energy between the electrons and nuclei in a hydrogen molecule, account being taken of the charge distribution in accordance with the wave theory. The term e^2/r_{AB} is the coulombic repulsion of the nuclei and, as already seen, J_1 represents the repulsion of the two electrons, while $-2J_2$ is the attractive energy between each electron and the nucleus with which it is not immediately associated. The attraction between the electron and the nucleus with which it is associated is, of course, included in E_0 . The quantity E_c (or, actually, $E_c - 2E_0$) is thus referred to as the *coulombic energy*; the term coulombic integral, which has previously been used for the matrix component H_{II} , can thus be justified.

17b. Resonance Energy in the Hydrogen Molecule.—Since the coulombic energy E_c is but a small fraction of the total potential energy at equilibrium (Fig. 9), it follows that the coulombic energy makes only a small contribution to the total binding energy of a normal hydrogen molecule. It is apparent, therefore, if there were no possibility of the exchange of electrons between the two nuclei, the stable hydrogen molecule, as it is known to the chemist, would not exist. Since the expression for the energy E_s , corresponding (approximately) to the stable molecule, involves the terms $H_{II} + H_{III}$ [equation (15.14)], it is seen that the exchange integral H_{III} is very largely responsible for the energy of the bond in the normal hydrogen molecule. The corresponding energy quantity is called the *exchange energy* or, frequently, the *resonance energy*.¹⁰ It is defined as the difference between the total binding energy and the classical, or coulombic, energy. In the case of the normal hydrogen molecule in its equilibrium state, the exchange energy constitutes about 85 to 90 per cent of the binding energy, according to Sugiura's calculations.

It is desirable to emphasize here that there is no fundamental difference between coulombic and exchange energies. The whole of the binding energy of a molecule is due to electrostatic forces between electrons and nuclei.

¹⁰ The term "resonance" is used in this connection because quantum mechanical phenomena of this type can be treated by methods analogous to those used for a classical resonating system, such as two coupled harmonic oscillators of equal, or approximately equal, frequencies.

The classical treatment would lead to the coulombic terms only, and hence is obviously incomplete. The quantum mechanical approach to the problem provides additional terms which take into account the possibility of an interchange of electrons between the nuclei. These terms do not represent new forces, but they make allowance for factors not recognized by classical electrostatic theory.

It can be seen from the foregoing discussion that if a hydrogen molecule is represented by either one or other of the two structures $H_A(1)H_B(2)$ or $H_A(2)H_B(1)$, where the subscripts A and B indicate the two hydrogen nuclei and (1) and (2) are the two electrons, the energy calculated for the system will be (numerically) too low. A great improvement is effected by allowing for the possibility, when expressing the eigenfunction for the system, that both configurations are equally possible; this is, of course, the basis of the Heitler-London treatment. It has been seen, however, in Section 16b, that even better values for the energy are obtained by introducing ionic terms into the eigenfunction, that is, by taking into consideration the occurrence of the ionic structures $H_A^+H_B^-$ and $H_A^-H_B^+$. The allowance for these additional structures does not affect the coulombic energy, and hence they must all be regarded as contributing to the resonance energy. It may be concluded, therefore, that the stabilization of a molecular system, resulting from the inclusion of resonance energy, can be attributed to the possibility of two or more electronic arrangements in the given system. Each reasonable electronic structure then makes a contribution to the eigenfunction of the system as a whole, and this, in accordance with the variation theorem, leads to a lower value for the potential energy; this means a greater value for the total binding energy of the atoms, and hence implies an increase in the resonance energy.

17c. Resonance Energy in Other Molecules.—The general ideas of resonance developed in Section 17b have been extended to other molecules, mainly by Pauling and his collaborators,¹¹ and the results have proved of great importance in chemistry. Consider, in the first place, a diatomic molecule AA, in which the two atoms are identical. If the atom A is hydrogen-like in character or, in general, if it may be regarded as consisting effectively of a nucleus and a single electron, the occurrence of resonance is possible, just as with the hydrogen molecule. The two atoms will thus be held together by relatively strong forces in the molecule AA.

In the second place, it may be supposed that the two atoms are different, so that a molecule AB, made up of two nuclei, A and B, and two electrons, is being considered. If the two electrons are designated by (1) and (2), the two electronic configuration $A(1)B(2)$ and $A(2)B(1)$, with identical energies, will clearly be possible. The corresponding orbital functions will then contribute equally to the complete eigenfunction for the system. Further, ionic structures, such as A^+B^- and A^-B^+ , in which both electrons are associated

¹¹ For review, see Pauling, "The Nature of the Chemical Bond."

with the atom B or with A, respectively, will be possible. As a general rule, one or other of the two ionic forms will be in excess, depending on the relative electronegativities of the two atoms. The greater the difference in the electronegativities, the greater the probability of the occurrence of the appropriate ionic structure. Consequently, ionic terms will generally make a larger contribution to the eigenfunction of a molecule consisting of two dissimilar, than of similar or identical atoms. The binding energy of the molecule AB might thus be expected to be at least equal to, or frequently greater than, the mean binding energy of the molecules AA and BB. The difference between the actual energy of dissociation AB and the arithmetic, or better geometric (cf. Section 21b), mean of the dissociation energies of the symmetrical molecules AA and BB has been called the *ionic resonance energy* of the molecule AB. It has been found to be related to the relative electronegativities of the atoms A and B, as was to be anticipated.

In general, if any molecular system, irrespective of its nature, can be depicted by a number of different, reasonable electronic configurations, indicated by the letters, A, B, C, D, etc., the eigenfunction for the whole system may then be represented, to a first approximation, by

$$\psi = a\psi_A + b\psi_B + c\psi_C + d\psi_D + \dots, \quad (17.7)$$

where the coefficients a, b, c, d, \dots , are determined by the relative contributions of the various structures to the normal state of the molecule. If the energies of these structures are not very different, the coefficients will be of the same order, and each will enhance the stability of the system by making an appreciable contribution to the resonance energy. It is then the practice to say that the system *resonates between*, or *resonates among*, the various configurations A, B, C, D, etc. If the energy of any of the theoretically possible structures is considerably less (numerically), i.e., it is less stable, than the others, the corresponding coefficient in equation (17.7) will be small and it will have little or no effect on the resonance energy of the system. The value of this energy is defined as the difference between the actual binding (or dissociation) energy of the system and the energy of the individual structures. The approximate evaluation of the resonance energy of the hydrogen molecule, by the method of Heitler and London, has already been considered, and in later parts of this chapter estimates will be made of the resonance energies in other systems.

When a system is stabilized by resonance, the actual structure is not to be regarded as being represented by one or other of the configurations which contribute towards the complete orbital eigenfunction and the total energy; nor is it to be considered as involving a rapid oscillation or interchange from one structure to another. The situation is that the actual electron distribution (eigenfunction) of the molecule cannot be represented in terms of a single structural formula, but it can be approximated by treating it as the appropriately weighted combination of the electron distributions (eigenfunctions) corresponding to the several configurations A, B, C, etc.

ODD ELECTRON SYSTEMS

18a. The Hydrogen Molecule-Ion.¹²—It will be evident from the discussion in Sections 17b and 17c that the stability, and presumably bond formation, in a molecule such as AA or AB depends largely on the presence of two electrons, (1) and (2), so that the two equivalent resonating structures A(1)A(2) and A(2)A(1), or A(1)B(2) and A(2)B(1), are possible. This result is in agreement with the general concept of the two-electron bond, to

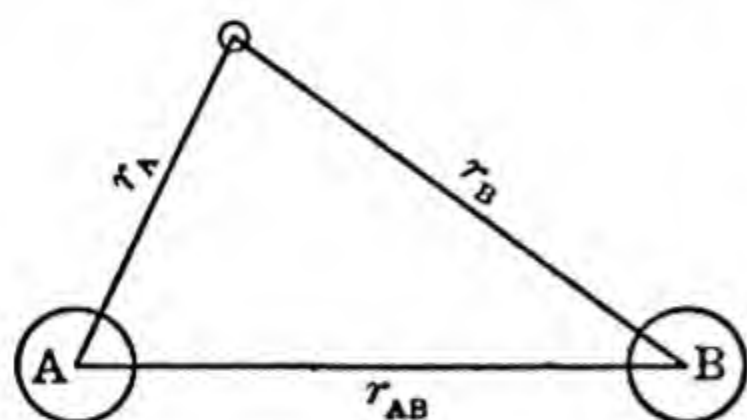


FIG. 10. The hydrogen molecule-ion system

which further reference will be made in Section 19c. It is important to consider, however, whether there are circumstances under which a single electron might serve to produce appreciable binding energy; this can best be done by an examination of the problem of the hydrogen molecule-ion, H_2^+ . This system consists of two identical hydrogen nuclei (A and B) and a single electron (Fig. 10). When the internuclear distance r_{AB} is large, there are two possible $1s$ orbitals for

the electron, which may be designated u_A and u_B ; these correspond to the association of the electron with nucleus A or nucleus B, respectively.

The variation method applied in the case of the hydrogen molecule can be used in connection with the hydrogen molecule-ion system. Writing ψ_I and ψ_{II} for the two orbitals, u_A and u_B , a trial eigenfunction would be given by $\psi = a_1\psi_I + a_2\psi_{II}$, as in equation (15.3). The secular equation for the present problem is then identical in form with equation (15.4). In reducing this to the form of equation (15.13) one adjustment has to be made, and this is in connection with the orthogonality integrals. These are represented by

$$\begin{aligned}\Delta_{I II} = \Delta_{II I} &= \int \psi_I \psi_{II} d\tau \\ &= \int u_A u_B d\tau,\end{aligned}\tag{18.1}$$

and this is equal to S [equation (15.66)]. The secular equation thus becomes

$$\begin{vmatrix} H_{II} - E & H_{I II} - SE \\ H_{I II} - SE & H_{II} - E \end{vmatrix} = 0,\tag{18.2}$$

and hence

$$E_S = \frac{H_{II} + H_{I II}}{1 + S}\tag{18.3}$$

and

$$E_A = \frac{H_{II} - H_{I II}}{1 - S}.\tag{18.4}$$

¹² Pauling and Wilson, ref. 1, Chap XII; Pauling, *Chem. Rev.*, 5, 173 (1928).

The corresponding eigenfunctions are then given by

$$\begin{aligned}\psi_S &= \frac{1}{\sqrt{2 + 2S}} (\psi_I + \psi_{II}) \\ &= \frac{1}{\sqrt{2 + 2S}} (u_A + u_B),\end{aligned}\quad (18.5)$$

and

$$\begin{aligned}\psi_A &= \frac{1}{\sqrt{2 - 2S}} (\psi_I - \psi_{II}) \\ &= \frac{1}{\sqrt{2 - 2S}} (u_A - u_B).\end{aligned}\quad (18.6)$$

Further, since there is now but one electron, the Hamiltonian operator for the H_2^+ system is simpler than that for the hydrogen molecule. The general form is the same as in equation (15.29), but V_A , V_B and V_0 , as well as the Laplacian operator, each contains terms for one electron only; it is thus readily seen that

$$H = -\frac{\hbar^2}{8\pi^2m} \nabla^2 - \frac{\epsilon^2}{r_A} - \frac{\epsilon^2}{r_B} + \frac{\epsilon^2}{r_{AB}}. \quad (18.7)$$

By employing methods exactly analogous to those described in Section 15c, it is found [cf. equation (15.37)], that the coulombic integral is

$$\begin{aligned}H_{II} &= \int u_A \left(E_0 + \frac{\epsilon^2}{r_{AB}} - \frac{\epsilon^2}{r_B} \right) u_A d\tau \\ &= E_0 + \frac{\epsilon^2}{r_{AB}} - J_2,\end{aligned}\quad (18.8)$$

where J_2 is defined by

$$J_2 = \epsilon^2 \int \frac{1}{r_B} (u_A)^2 d\tau. \quad (18.9)$$

The physical significance of this integral is the same as that of the integral J_2 in the hydrogen molecule problem; it represents the energy of interaction of the electronic charge distributed about one of the hydrogen nuclei with the positive charge of the other nucleus. Hence the value of J_2 in equation (18.8) is given [equation (15.55)] by

$$J_2 = \frac{\epsilon^2}{a_0 D} \{1 - e^{-2D}(1 + D)\}, \quad (18.10)$$

where, as before, D is the internuclear distance in atomic units, i.e., r_{AB}/a_0 . The expression for the exchange integral is

$$\begin{aligned}H_{I II} &= \int u_A \left(E_0 + \frac{\epsilon^2}{r_{AB}} - \frac{\epsilon^2}{r_B} \right) u_B d\tau \\ &= E_0 S + \frac{\epsilon^2}{r_{AB}} S - K,\end{aligned}\quad (18.11)$$

where

$$S = \int u_A u_B d\tau \quad (18.12)$$

and

$$K = \epsilon^2 \int \frac{1}{r_B} (u_A u_B) d\tau. \quad (18.13)$$

Comparison of equations (18.12) and (18.13) with equations (15.66) and (15.65), shows immediately the identity of the K and S terms in the two cases; hence, for the present problem, by equations (15.72) and (15.74),

$$K = \frac{\epsilon^2}{a_0} e^{-D} (1 + D) \quad (18.14)$$

and

$$S = e^{-D} (1 + D + \frac{1}{3} D^2). \quad (18.15)$$

Combination of equations (18.8) and (18.11) for H_{II} and H_{III} , respectively, with equations (18.3) and (18.4) for E_S and E_A , then gives

$$E_S - E_0 = \frac{\epsilon^2}{r_{AB}} - \frac{J_2 + K}{1 + S} \quad (18.16)$$

and

$$E_A - E_0 = \frac{\epsilon^2}{r_{AB}} - \frac{J_2 - K}{1 - S}. \quad (18.17)$$

Since J_2 , K and S are known in terms of the internuclear distance, it is possible to calculate the values of $E_S - E_0$ and $E_A - E_0$, representing the potential energies (or binding energies) corresponding to the symmetric and antisymmetric electron eigenfunctions, respectively, as a function of r_{AB} . The results obtained are quite similar to those for the hydrogen molecule (see Fig. 33); the antisymmetric orbital leads to an unstable, repulsive state, but the symmetric function gives a potential energy curve with a minimum, implying a stable form of the hydrogen molecule-ion. The value of the potential energy at the minimum indicates a dissociation energy of 40.7 kcal. per mole.

The foregoing treatment, like the Heitler-London treatment of the hydrogen molecule, is very approximate, but the use of various refinements leads to value of 63.8 kcal. for the energy of the H_2^+ ion, in close agreement with the result obtained from spectroscopic data. The single electron in the hydrogen molecule-ion has thus a considerable bonding effect, and it is of interest to see how this binding energy arises. If the electron had been regarded as attached to one or the other of the two nuclei, the eigenfunction would have been u_A or u_B only, and not a combination of the two. The energy would then have been the coulombic portion only (E_C), approximately equal to H_{II} , assuming the orthogonality integral S to be zero; thus

$$E_C - E_0 = \frac{\epsilon^2}{r_{AB}} - J_2. \quad (18.18)$$

The coulombic binding energy calculated from equation (18.18) for the hydrogen molecule-ion is not significantly different from zero; in fact, if anything, the results indicate repulsion at all internuclear distances. It follows, therefore, that the whole of the bonding effect of the single electron in H_2^+ is to be attributed to the fact that the true eigenfunction of the system is more closely approximated by a linear combination of u_A and u_B , than by either alone. In other words, the resonance energy, or exchange energy, which arises because of the identity of the electron configurations H_AH_B^+ , in which the electron is associated with the hydrogen nucleus A, and H_A^+H_B , in which it is associated with B, is the sole cause of the stability of the H_2^+ ion.

18b. Odd-Electron Bonds.¹³—The conclusion just reached may be extended to other cases. It can be seen that whenever there are two identical nuclei A and a single electron, resonance between the equivalent structures $\text{A}^+ \cdot \text{A}$ and $\text{A} \cdot \text{A}^+$, where the dot represents the electron, is possible. In other words, molecule-ions of the general type A_2^+ should have appreciable stability. Turning now to the case of two different nuclei A and B, with one electron, the two possible structures, $\text{A}^+ \cdot \text{B}$ and $\text{A} \cdot \text{B}^+$, are no longer equivalent. If the atoms A and B are somewhat similar, so that the energies of the two structures do not differ greatly, the eigenfunctions of both will contribute appreciably to that of the system as a whole. Under these conditions resonance will occur, and the single electron will exert a definite bonding effect. The circumstances are then quite similar to those arising in the case of the A_2^+ ion. On the other hand, if the energies of the structures $\text{A}^+ \cdot \text{B}$ and $\text{A} \cdot \text{B}^+$ are considerably different, the eigenfunction for the system will consist almost exclusively of the contribution of the most stable form. The energy will then be coulombic in nature with little, if any, resonance energy and the system will have a very small, or zero, binding energy. If A and B are appreciably different, therefore, the molecule ion $(\text{AB})^+$ will be unstable. A relatively strong one-electron bond should thus be possible only when the two structures resulting from the attachment of the electron to one nucleus or the other have energies which are almost, or actually, identical.

The arguments concerning the bonding effect of a single electron may be extended to the case of three electrons and two nuclei. Here again, if the two nuclei are the same, the two states $\text{A} \vdots \text{A}^+$ and $\text{A}^+ \vdots \text{A}$ have equal energies; resonance is thus possible and there will be an appreciable binding energy. It is of interest to note that the calculations have actually been carried out for the helium molecule-ion, He_2^+ , consisting of two (identical) helium nuclei and three electrons. The binding energy, which is due exclusively to the resonance energy contribution, is about 57.5 kcal. per mole, and so this ion has appreciable stability. If the two nuclei are appreciably different, resonance will no longer be possible because of the energy difference of the two electronic configurations. The three electrons should then have little or no bonding effect in a system such as $\text{A} \vdots \text{B}$, where A and B are neither the same

¹³ Pauling, *J. Am. Chem. Soc.*, 53, 3225 (1931).

nor similar. A case in point is the molecule HeH, which is made up of two dissimilar nuclei, one of helium and one of hydrogen, and three electrons. Calculations show that this molecule can occur only in a repulsive (unstable) state.

SPIN EIGENFUNCTIONS

19a. The Pauli Principle.—The electron eigenfunctions that have been considered so far, both in the present and the preceding chapter, have excluded the effect of the so-called electronic spin; it is because they are concerned only with orbital motion that they have been referred to as orbitals. The complete eigenfunction of an electron must include a contribution for the spin, and a satisfactory solution is to take the former as being equal to the product of the orbital eigenfunction and of an eigenfunction representing the orientation of the spin axis of the electron. This separation into two independent parts is justifiable because there is apparently only slight interaction between spin and orbital momenta. Consequently, these two forms of angular momentum, and the corresponding eigenfunctions, may be regarded as independent; the complete eigenfunction may thus be taken as equal to the product of the separate orbital and spin functions. If ψ is the orbital of an electron in an atom for a given value of the quantum numbers n , l and m_l , then according to the Pauli principle (see Section 1c), the spin eigenfunction may be represented only by α or β , corresponding to values of $+\frac{1}{2}$ or $-\frac{1}{2}$ for m_s , the spin quantum number. The complete electron eigenfunction can then be either $\psi\alpha$ or $\psi\beta$.

Imagine a system consisting of two electrons (1) and (2), for which there are available the orbitals u_a and u_b . Following the treatment applied in the case of the hydrogen molecule, two orbital eigenfunctions are possible for the system, viz.,

$$\psi_S = c_S \{u_a(1)u_b(2) + u_a(2)u_b(1)\} \quad (19.1)$$

and

$$\psi_A = c_A \{u_a(1)u_b(2) - u_a(2)u_b(1)\}, \quad (19.2)$$

where c_S and c_A are the normalization factors. The complete eigenfunctions may then be obtained by multiplying ψ_S and ψ_A by the spin eigenfunctions for the two electrons. There are four possible values for the latter, depending on whether the spin quantum number m_s of the electron is $+\frac{1}{2}$ (spin eigenfunction = α) or $-\frac{1}{2}$ (spin eigenfunction = β), as indicated below.

$m_s(1)$	$m_s(2)$	$\sum m_s$	Eigenfunction
$+\frac{1}{2}$	$+\frac{1}{2}$	1	$\alpha(1)\alpha(2)$
$+\frac{1}{2}$	$-\frac{1}{2}$	0	$\alpha(1)\beta(2)$
$-\frac{1}{2}$	$+\frac{1}{2}$	0	$\beta(1)\alpha(2)$
$-\frac{1}{2}$	$-\frac{1}{2}$	-1	$\beta(1)\beta(2)$

The second and third of these spin eigenfunctions clearly represent equivalent states, differing only in the interchange of the electrons; this particular

state is consequently doubly degenerate. The actual spin eigenfunctions, when the degeneracy is removed, may be taken as linear combinations, represented by the sum and difference, of the two eigenfunctions given in the tabulation, viz.,

$$\frac{1}{\sqrt{2}} \{ \alpha(1)\beta(2) + \beta(1)\alpha(2) \} \quad \text{and} \quad \frac{1}{\sqrt{2}} \{ \alpha(1)\beta(2) - \beta(1)\alpha(2) \},$$

the factor $1/\sqrt{2}$ being introduced for normalization. It will be observed that these combinations of the two eigenfunctions for equivalent states are quite similar to those obtained for the orbitals in the hydrogen molecule problem [cf. equations (15.26) and (15.28), and equations (19.1) and (19.2)].

Upon multiplying the two orbital eigenfunctions ψ_S and ψ_A by the four spin eigenfunctions, there result eight complete eigenfunctions, which may be written as follows:

$$\begin{aligned} \psi_1 &= \psi_S \{ \alpha(1)\alpha(2) \} \\ \psi_2 &= \psi_S \{ \alpha(1)\beta(2) + \beta(1)\alpha(2) \} / \sqrt{2} \\ \psi_3 &= \psi_S \{ \alpha(1)\beta(2) - \beta(1)\alpha(2) \} / \sqrt{2} \\ \psi_4 &= \psi_S \{ \beta(1)\beta(2) \} \\ \psi_5 &= \psi_A \{ \alpha(1)\alpha(2) \} \\ \psi_6 &= \psi_A \{ \alpha(1)\beta(2) + \beta(1)\alpha(2) \} / \sqrt{2} \\ \psi_7 &= \psi_A \{ \alpha(1)\beta(2) - \beta(1)\alpha(2) \} / \sqrt{2} \\ \psi_8 &= \psi_A \{ \beta(1)\beta(2) \} \end{aligned}$$

Without further information it is not possible to state whether these eigenfunctions are significant; however, such information is provided by spectroscopic studies. In order to account for the spectrum of atomic helium, it is necessary to make a postulate which may be stated in the ensuing general form: *The complete eigenfunction of a system of two or more electrons must be antisymmetric in every pair of electrons.* That is to say, if the coordinates of any two electrons are interchanged there must always be a reversal in the sign of the complete eigenfunction. The product of two symmetric or of two antisymmetric functions is always symmetric, but the product of a symmetric and an antisymmetric function is antisymmetric. Consequently, it is immediately seen that of the eight complete eigenfunctions recorded above, ψ_3 , ψ_5 , ψ_6 and ψ_8 are antisymmetric; these are the only permitted eigenfunctions for the system of two electrons. It may be noted that when the two orbitals u_a and u_b available for the two electrons are identical, that is, when the quantum numbers n , l and m_l are the same for both electrons, ψ_5 , ψ_6 and ψ_8 become zero. The only possible eigenfunction is then ψ_3 , which corresponds to a state in which the two electrons have opposite spins. The postulate concerning the antisymmetric nature of the complete eigenfunction of a system of two or more electrons thus leads to the same conclusion as does the Pauli principle; it is, in fact, regarded as the quantum mechanical equivalent of the exclusion principle.

19b. The Hydrogen Molecule.—If the arguments just presented are considered in relation to the hydrogen molecule, it is apparent that there are four possible complete eigenfunctions of the system; these are equivalent to ψ_3 , ψ_5 , ψ_6 and ψ_8 given above, viz.,

$$\begin{array}{ll} \psi_S \{ \alpha(1)\beta(2) - \beta(1)\alpha(2) \} / \sqrt{2} & \sum m_s = 0 \quad {}^1\Sigma_g^+ \text{ state} \\ \psi_A \{ \alpha(1)\alpha(2) \} & + 1 \\ \psi_A \{ \alpha(1)\beta(2) + \beta(1)\alpha(2) \} / \sqrt{2} & 0 \quad \left. \vphantom{\begin{array}{l} + 1 \\ 0 \end{array}} \right\} {}^3\Sigma_u^+ \text{ state.} \\ \psi_A \{ \beta(1)\beta(2) \} & - 1 \end{array}$$

It follows, therefore, that there is only one state of molecular hydrogen with the symmetric orbital wave function, which as already seen is the stable, or attractive, form of this substance. On the other hand, there are three states of the unstable, or repulsive, form with the antisymmetric orbital eigenfunction. The stable form of molecular hydrogen is thus a singlet state and the unstable form is a triplet; it will be seen in Chapter VI that the term symbols for these states are ${}^1\Sigma_g^+$ and ${}^3\Sigma_u^+$, respectively. The three levels constituting the triplet state have almost identical energies, and differ only in the values of $\sum m_s$, the resultant electron spin quantum number, which can be +1, 0 and -1, respectively.

19c. Electron Spin and Valence.—It will be observed that in the stable form of the normal hydrogen molecule the resultant electron spin is zero. The formation of a stable molecule can thus occur only by the coupling of the two electrons with opposite spins. This conclusion led London¹⁴ to suggest that the formation of a valence bond, in general, resulted when an electron from one atom was able to pair with an electron having an opposed spin, provided by another atom. The tendency for electrons from different atoms to pair up in this manner thus provides a theoretical basis for the electron pair bond postulated by G. N. Lewis on empirical grounds. According to this view, the valence of an atom would be equal to the number of unpaired electrons it contained. It would be necessary to suppose, therefore, that in certain cases there is an "unpairing" of electrons as a preliminary to chemical combination. The normal (3P) carbon atom, for example, has in its L shell (principal quantum number $n = 2$) four electrons, of which two have their spins paired while two are unpaired, viz., $2s^2 2p^2$. The normal carbon atom should thus have a valence of two. Such a valence is, of course, uncommon, and so it must be supposed that in chemical reaction the normal carbon atom is first raised to an excited (5S) state, viz., $2s 2p^3$, in which the spins of all four electrons are uncoupled, so that a valence of four is possible.

Further light may be thrown on certain aspects of chemical valence by considering the distribution of the electronic charge density around the two nuclei, for the two forms of molecular hydrogen, with symmetric and antisymmetric orbital eigenfunctions, respectively. The charge density may be evaluated from the square of the eigenfunctions, viz., ψ_S^2 and ψ_A^2 , using equations (15.26) and (15.28) to define ψ_S and ψ_A , and employing the 1s

¹⁴ London, *Z. Physik*, 46, 455 (1928).

orbital eigenfunctions of atomic hydrogen for $u_A(1)$, $u_B(2)$, etc. It is thus possible to calculate the values of ψ_S^2 and ψ_A^2 for various distances between the electrons and the two hydrogen nuclei. The results may be plotted in the form of a series of contour lines of equal electronic charge density, as shown in Fig. 11; the numbers against the various contour lines give the relative values of the charge densities. From these diagrams it is at once apparent that in the stable form of molecular hydrogen, the charge density

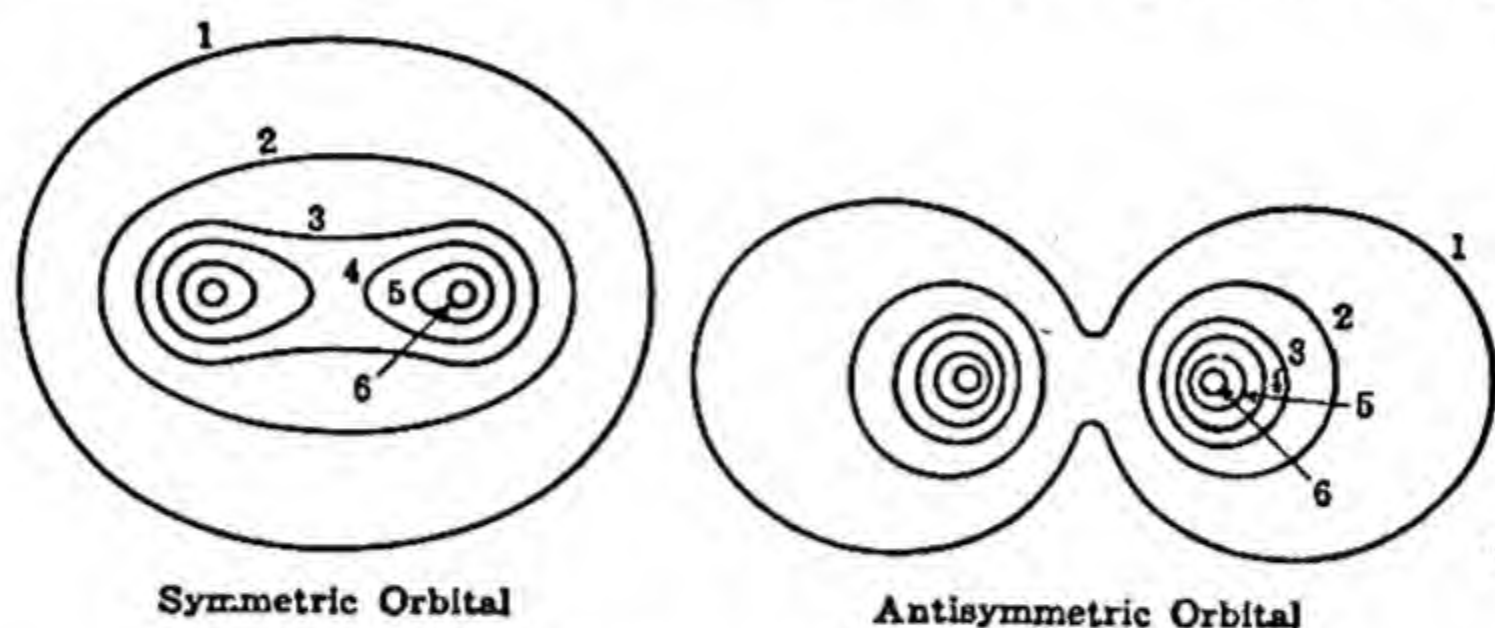


FIG. 11. Electron charge densities for hydrogen molecule

in the region between the two nuclei is high, but in the unstable form it is exceptionally low in this vicinity. It may be concluded, therefore, that in the formation of a bond between two hydrogen atoms, the electrons, with opposite spins, tend to concentrate in the space between the nuclei. The general extension of this conclusion to other cases forms the basis of what has become known as the *method of localized pairs* for the quantum mechanical study of valence.

19d. Interaction Energy of Electrons.—When two electrons situated on different hydrogen atoms come together, their spins, as implied in Section 19a, can couple in four ways; the resultant values of $\sum m_s$ being $+1$, 0 (twice), and -1 . One of these ways, $\sum m_s = 0$, corresponds to that in the $^1\Sigma_g^+$ state of molecular hydrogen with the symmetric orbital eigenfunction ψ_S . The other three spin combinations, $\sum m_s = +1$, 0 and -1 , correspond to the $^3\Sigma_u^+$ state, in which the orbital eigenfunction ψ_A is antisymmetric. Since all four types of coupling have equal probability, it follows that one fourth of the encounters between two hydrogen atoms will lead to the formation of molecules in the singlet state, the other three fourths leading to the triplet form. Similar conditions will hold when two electrons, each situated on a different hydrogen *molecule*, approach one another. At any instant there will be a proportion of one electron pair in a singlet ($^1\Sigma$) state to three pairs in the triplet ($^3\Sigma$) state. The average interaction energy E_I of two *non-bonded* hydrogen atoms, on different molecules, will thus be given by

$$E_I = \frac{1}{4}(E_S + 3E_A), \quad (19.3)$$

where, as before, E_S is the energy of the $^1\Sigma$ state, i.e., with symmetric

orbital eigenfunction, and E_A is that of the $^3\Sigma$ state, i.e., with antisymmetric orbital.

If the orthogonality integral S^2 is assumed to be zero, equation (15.14) gives the value of E_S as

$$E_S = H_{I I} + H_{I II}, \quad (19.4)$$

and this may be written

$$E_S = Q + J, \quad (19.5)$$

where Q , equal to $H_{I I}$, represents the coulombic energy, and J , equal to $H_{I II}$, is the exchange energy. The quantity E_S is, of course, the value of the interaction energy of the electrons in two bonded hydrogen atoms. Similarly, it follows, again neglecting nonorthogonality, that

$$\begin{aligned} E_A &= H_{I I} - H_{I II} \\ &= Q - J, \end{aligned} \quad (19.6)$$

and so, from equations (19.3), (19.5) and (19.6),

$$E_I = Q - \frac{1}{2}J, \quad (19.7)$$

which is the interaction energy of two electrons on nonbonded hydrogen atoms. Attention may be called to the fact that since the numerical value of $\frac{1}{2}J$ almost invariably exceeds that of Q , both of which are negative, the value of E_I will be positive, which implies repulsion between atoms not connected by a valence bond.

If the results obtained above are extended to a system consisting of a number of electrons, coupled in pairs with opposite spins to form localized bonds, it follows that the energy E_b of the bonded electrons may be represented by

$$E_b = \sum_i (Q_{ii} + J_{ii}), \quad (19.8)$$

by analogy with equation (19.5), while the energy E_n of nonbonded electrons, by analogy with equation (19.7), is

$$E_n = \sum_{ij} (Q_{ij} - \frac{1}{2}J_{ij}), \quad \text{for } i \neq j. \quad (19.9)$$

The subscript ii refers to every pair of electrons coupled as a bond, and ij to all pairs of nonbonded electrons. The total energy E is then the sum of E_b and E_n ; hence,

$$E = Q + \sum_i J_{ii} - \frac{1}{2} \sum_{ij} J_{ij}, \quad (19.10)$$

where Q is now the total coulombic energy for the interaction of every electron pair.

Emphasis should be laid on some of the approximations involved in the derivation of equation (19.10). In the first place, it has been supposed that the atomic orbitals of the electrons on different nuclei are mutually or-

thogonal; in the second place, it should be realized that the exchange integrals, J_{ii} and J_{ij} , do not take into account the possibility that more than two electrons are interchanged at one time. A more exact treatment of this subject will be given later (Section 24).

METHOD OF DIRECTED VALENCE BONDS

20a. Direction of Valence Bonds.—The conclusions drawn from the approximate Heitler-London treatment of the hydrogen molecule, that the formation of a valence bond is accompanied by the coupling of the spins of unpaired electrons from different atoms and that the electrons tend to concentrate in the region between the nuclei, has been extended by Slater,¹⁵ and particularly by Pauling,¹⁶ to yield results of considerable interest to chemists. The method of treatment has become known as either the *method of localized pairs* or the *method of directed valence bonds*.¹⁷ The essential postulates are as follows: (a) a single bond is formed by the interaction of two unpaired electrons of opposite spin derived from different atoms; (b) the direction of the bond will correspond to that in which the orbital wave functions of these two electrons overlap as much as possible; and (c) of two orbitals in an atom the one which can overlap more with the orbital of another atom will form the stronger bond with that atom. Some theoretical justification for the second of these postulates will be given later.

It was seen in Section 13h that the radial portions of s and p orbital eigenfunctions of hydrogen-like atoms are approximately the same, but their dependence on the angle θ varies. In general, s orbitals are spherically symmetrical and consequently, in accordance with the postulates enunciated above, s electrons will have no directional valence effect. With p electrons, however, there are three possible orbitals, p_x , p_y and p_z , consisting of double spheres with their long axes oriented in three directions along the rectangular axes x , y and z , respectively, i.e., at right angles to each other (see Fig. 6). It follows, therefore, that when an atom forms bonds involving p electrons, the angle between these bonds should be 90° .

20b. Bond Angles.—The oxygen atom has six electrons in the K shell, two of which are paired $2s$ electrons, i.e., with opposite spins, two others are paired $2p$ electrons, while the remaining two are unpaired $2p$ electrons occupying separate orbitals, e.g., p_x and p_y . If a hydrogen atom is brought up to the oxygen, it will attach itself in such a way as to result in the maximum overlap of the $1s$ orbital of the former with one of the $2p$ orbitals, e.g., $2p_x$, of the latter atom. The hydrogen will thus be located along the x axis of the oxygen atom. When a second hydrogen atom is brought up, its orbital will tend to overlap with the $2p_y$ orbital of the oxygen atom, and so it will become attached along the y axis. The angle between the two O—H bonds

¹⁵ Slater, *Phys. Rev.*, **37**, 481 (1931); **38**, 325 (1931).

¹⁶ Pauling, ref. 11; *J. Am. Chem. Soc.*, **53**, 1367 (1931); Hultgren, *Phys. Rev.*, **40**, 891 (1932).

¹⁷ It is sometimes also referred to as the H-L-S-P method, from the initials of Heitler, London, Slater and Pauling who are chiefly responsible for its development.

in the water molecule should thus be 90° . The experimental value is $104^\circ 31'$ (Section 38b), and the discrepancy must undoubtedly be attributed mainly to the repulsion between the hydrogen atoms for which no allowance has been made. In hydrogen sulfide, H_2S , the two hydrogen atoms are further apart than in water, because the sulfur atom is larger than oxygen, and hence the mutual repulsion is less; the bond angle is here found to be $92^\circ 20'$.

The nitrogen atom has three p orbitals that are available for bond formation, and hence the angles between the three N—H bonds in ammonia should be 90° . The observed angle is reported to be 108° , the increase over the theoretical value being, again, due to repulsion of the hydrogen atoms. In crystalline arsenic, antimony and bismuth, where bonds between p orbitals are involved, the bond angles are 97° , 96° and 94° , respectively. It is of interest to record that the directed valence bond treatment predicts a pyramidal, rather than a planar, arrangement for compounds of the type RX_3 , where R is nitrogen or other member of the nitrogen group of elements; this is, of course, in agreement with experiment.

20c. Hybridized Bond Eigenfunctions.—The normal carbon atom has, according to its spectrum, two paired $2s$ and two unpaired $2p$ electrons in its outer shell; only the latter should be available for bond formation, and so a valence of two might be expected. Since carbon is normally quadrivalent, it must be postulated that in carbon compounds the atom is in an excited state with one s and three p electrons, all with unpaired spins (cf. Section 19c). According to the arguments in the preceding section, it might be supposed that quadrivalent carbon should have three bonds at right angles, formed with the three p orbitals, and a fourth bond, using the s orbital, having no definite direction. Chemists have long known, however, that the four bonds of the carbon atom are arranged tetrahedrally, and it is desirable to see how this fact can be correlated with quantum mechanical requirements.

It has been seen earlier that the eigenfunction of the normal state of a system is in general a linear combination of a number of orbitals of states of similar energies; the best combination is the one that minimizes the energy or, in terms of valence bonds, the one that gives the maximum bond strength. The carbon atom has available one s orbital and three p orbitals (p_x , p_y and p_z), and if these have energies that are not greatly different, the four bond-forming eigenfunctions for the whole system, which are linear combinations of the single electron orbitals, may be written in the general form

$$\psi_i = a_i s + b_i p_x + c_i p_y + d_i p_z, \quad (20.1)$$

where i is 1, 2, 3 or 4. The coefficients a_i , b_i , c_i and d_i are determined by the normalization condition

$$\int \psi_i^* \psi_i d\tau = \int \psi_i^2 d\tau = 1,$$

or

$$a_i^2 + b_i^2 + c_i^2 + d_i^2 = 1, \quad (20.2)$$

and by the orthogonality requirement

$$\int \psi_i \psi_k d\tau = 0.$$

or

$$a_i a_k + b_i b_k + c_i c_k + d_i d_k = 0, \quad (20.3)$$

where i and k are 1, 2, 3 and 4 but $i \neq k$. The relative values of the eigenfunctions s , p_x , p_y and p_z are given in Table V (page 60); they are 1; $\sqrt{3} \sin \theta \cos \phi$, $\sqrt{3} \sin \theta \sin \phi$ and $\sqrt{3} \cos \theta$, respectively.

The direction of the first bond eigenfunction is immaterial, and so it may be chosen to lie along the x axis; in this direction p_y and p_z are zero, and hence equation (20.1) becomes, for $i = 1$,

$$\psi_1 = a_1 s + b_1 p_x, \quad (20.4)$$

and since by equation (20.2)

$$a_1^2 + b_1^2 = 1,$$

it follows that

$$\psi_1 = a_1 s + \sqrt{1 - a_1^2} p_x. \quad (20.5)$$

It is now required to find the value of a that makes the energy a minimum, and hence the bond strength a maximum. According to the postulates in Section 20a, this will presumably be the condition that makes the eigenfunction a maximum in the bond direction, that is, along the x axis. The values of s and p_x in the x direction are 1 and $\sqrt{3}$, respectively ($\phi = 90^\circ$, $\theta = 0^\circ$); hence the value of the eigenfunction ψ_1 , is given by

$$\psi_1 = a_1 + \sqrt{3}(1 - a_1^2). \quad (20.6)$$

The maximum is then found by differentiating with respect to a_1 and equating to zero; this leads to

$$a_1 = \frac{1}{2} \quad \text{and} \quad b_1 = \frac{1}{2}\sqrt{3}. \quad (20.7)$$

Insertion of these results in equation (20.4) gives for the best eigenfunction

$$\psi_1 = \frac{1}{2}s + \frac{1}{2}\sqrt{3}p_x. \quad (20.8)$$

Taking s as equal to 1.0 and p_x as $\sqrt{3}$, in the x direction, the maximum value of ψ_1 , which is in the x direction, is seen to be equal to 2.0; this is appreciably greater than $\sqrt{3}$; i.e., 1.732, the maximum value of the p_x orbital. The particular combination of s and p_x eigenfunctions given by equation (20.8) is thus a better approximation than either s or p_x orbitals alone. A plot of the function ψ_1 , in the xz plane, is shown in Fig. 12.

Attention may now be turned to the second bond eigenfunction, ψ_2 ; this may be chosen as having its maximum in the xz plane, so that the orbital p_y makes no contribution. The expression for ψ_2 then takes the form

$$\psi_2 = a_2 s + b_2 p_x + d_2 p_z. \quad (20.9)$$

Since the maximum lies in the xz plane, the angle ϕ must be 0° or 180° (cf. Fig. 4); the value $\phi = 0^\circ$ gives the positive portion of the p_x orbital contributing to ψ_1 , and so the negative portion, with $\phi = 180^\circ$, must be employed for ψ_2 . Hence, $\cos \phi$ is equal to -1 , and p_x becomes $-\sqrt{3} \sin \theta$;

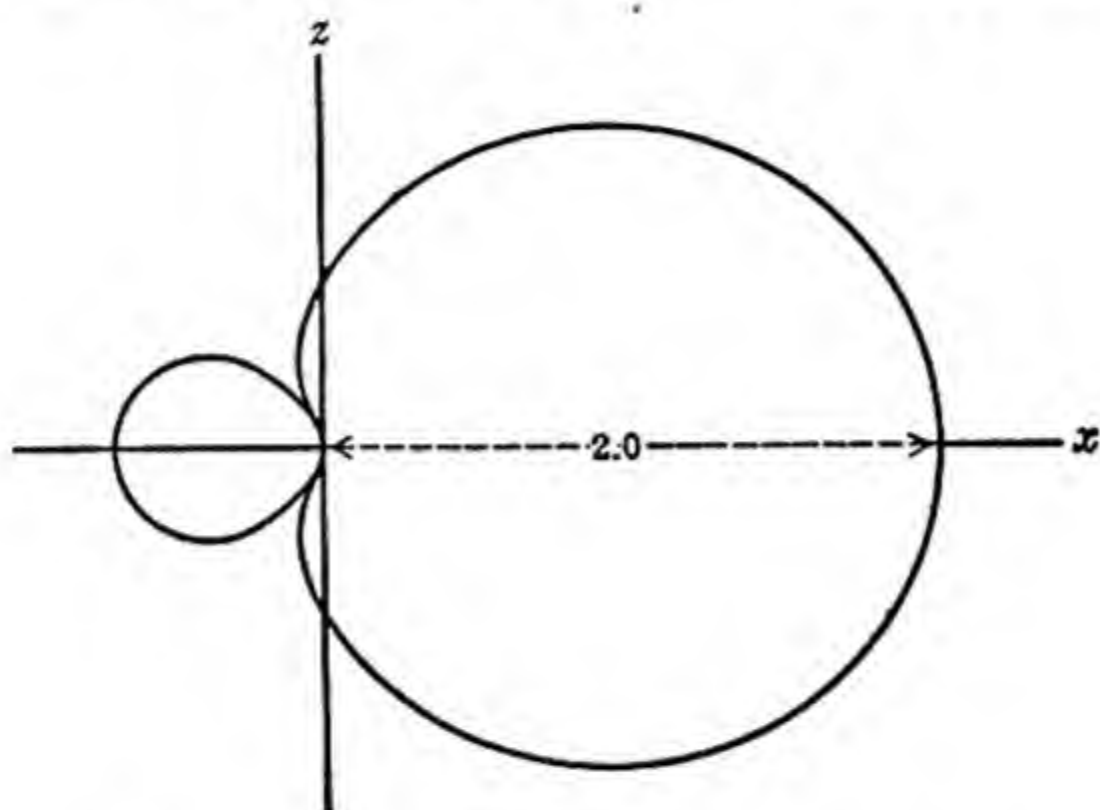


FIG. 12. Hybridized sp eigenfunction

since $s = 1$ and $p_x = \sqrt{3} \cos \theta$, as given above, it follows that

$$\psi_2 = a_2 - b_2\sqrt{3} \sin \theta + d_2\sqrt{3} \cos \theta. \quad (20.10)$$

The normalization condition is

$$a_2^2 + b_2^2 + d_2^2 = 1,$$

and for orthogonality

$$a_1a_2 + b_1b_2 = 0,$$

since d_1 is zero. Utilizing the values of a_1 and b_1 already derived, it is found that

$$a_2 = -b_2\sqrt{3} \quad \text{and} \quad d_2 = \sqrt{1 - 4b_2^2}, \quad (20.11)$$

and hence

$$\psi_2 = -b_2\sqrt{3}(1 + \sin \theta) + \sqrt{3}(1 - 4b_2^2) \cos \theta. \quad (20.12)$$

In order to find the values of b_2 and θ that make ψ_2 a maximum, the derivatives of ψ_2 , as given by equation (20.12), with respect to b_2 and θ are equated to zero. Upon solving the simultaneous equations, it is found that

$$b_2 = -\frac{1}{2\sqrt{3}} \quad \text{and} \quad \sin \theta = \frac{1}{3}, \quad (20.13)$$

and hence $\theta = 19^\circ 28'$. Inserting these results into equation (20.12), the maximum value of ψ_2 , like that of ψ_1 , is seen to be 2.0. Further, since θ is $19^\circ 28'$ and ϕ is 180° , it is evident that the direction of the maximum of the bond eigenfunction ψ_2 makes an angle of $90^\circ + 19^\circ 28' = 109^\circ 28'$ with the x axis, that is, with the direction of the maximum of the first bond eigen-

function ψ_1 . In other words, according to the postulates given above, the angle between the two carbon atom bonds whose eigenfunctions are ψ_1 and ψ_2 is exactly equal to the regular tetrahedral angle, in agreement with the views generally accepted for this atom.

Having found the best value for b_2 , it is readily seen from equation (20.11) that

$$a_2 = \frac{1}{2} \quad \text{and} \quad d_2 = \frac{\sqrt{2}}{\sqrt{3}}, \quad (20.14)$$

and insertion of these results, together with that for b_2 , in equation (20.9) gives

$$\psi_2 = \frac{1}{2}s - \frac{1}{2\sqrt{3}}p_x + \frac{\sqrt{2}}{\sqrt{3}}p_z. \quad (20.15)$$

By means of arguments similar to the foregoing, it can be shown that the other two eigenfunctions of the carbon atom are

$$\psi_3 = \frac{1}{2}s - \frac{1}{2\sqrt{3}}p_x + \frac{1}{\sqrt{2}}p_y - \frac{1}{\sqrt{6}}p_z \quad (20.16)$$

and

$$\psi_4 = \frac{1}{2}s - \frac{1}{2\sqrt{3}}p_x - \frac{1}{\sqrt{2}}p_y - \frac{1}{\sqrt{6}}p_z. \quad (20.17)$$

These, like ψ_1 and ψ_2 , have maximum values of 2.0 in directions making tetrahedral angles with each other, and with those of the other two bond eigenfunctions. It is clear, therefore, that the combination, or *hybridization*, of s and p orbitals, leading to the formation of what have been called *tetrahedral orbitals*, provides the quantum mechanical basis for the familiar tetrahedral carbon atom as it occurs in diamond and in aliphatic compounds. It is probable that the bond angles will have the exact regular tetrahedral value only when four identical atoms or groups are attached to the carbon atom. When the groups are different, the angles may possibly differ to a slight extent from the ideal value of $109^\circ 28'$.

20d. Trigonal Bonding Eigenfunctions.—It has been seen that when there is no sp hybridization, the p electrons can form three equivalent bonds at right angles to one another; on the other hand, when such hybridization does occur, the strongest bonds are tetrahedral. A further possibility which may be considered is sp hybridization leading to the formation of three equivalent (trigonal) bond eigenfunctions whose maxima lie in one plane, the directions making angles of 120° with each other. If this plane is chosen as the xy plane, there will be no contribution from the p_x eigenfunctions, and so it is necessary to consider only combinations of s and p_y and p_z orbitals.

Starting with the eigenfunction ψ_1 , with its maximum in the x direction, then

$$\psi_1 = as + bp_x, \quad (20.18)$$

where a represents the portion of the s orbital and b that of the p_z orbital that contribute to ψ_1 . The s orbital may be regarded as divided equally among the three eigenfunctions, ψ_1 , ψ_2 and ψ_3 , and so the coefficient of s will be the same in each case. In order to find the coefficients of the other single electron orbitals, the negative part of the p_z orbital and both parts of the

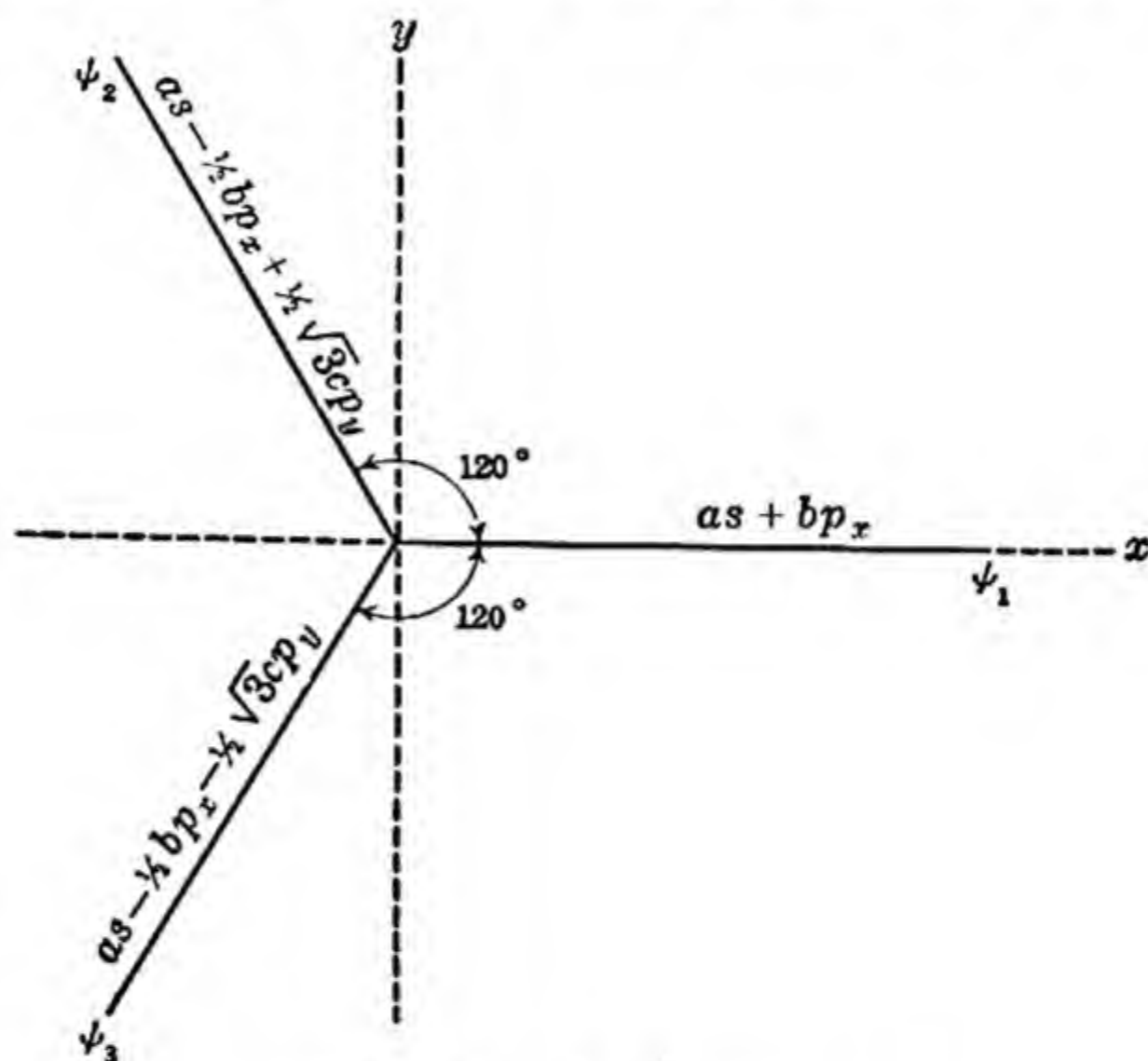


FIG. 13. Trigonal sp eigenfunctions

p_y orbital are resolved along the two directions making angles of 120° with the x axis, as shown in Fig. 13. It is then possible to write

$$\psi_2 = as - \frac{1}{2}bp_z + \frac{1}{2}\sqrt{3}cp_y \quad (20.19)$$

and

$$\psi_3 = as - \frac{1}{2}bp_z - \frac{1}{2}\sqrt{3}cp_y. \quad (20.20)$$

Making use of the normalization and orthogonality conditions, it is found that

$$a = \frac{1}{\sqrt{3}}, \quad b = \frac{\sqrt{2}}{\sqrt{3}} \quad \text{and} \quad c = \frac{\sqrt{2}}{\sqrt{3}}, \quad (20.21)$$

and hence the three hybridized trigonal eigenfunctions are

$$\psi_1 = \frac{1}{\sqrt{3}}s + \frac{\sqrt{2}}{\sqrt{3}}p_z, \quad (20.22)$$

$$\psi_2 = \frac{1}{\sqrt{3}}s - \frac{1}{\sqrt{6}}p_z + \frac{1}{\sqrt{2}}p_y \quad (20.23)$$

and

$$\psi_3 = \frac{1}{\sqrt{3}} s - \frac{1}{\sqrt{6}} p_x - \frac{1}{\sqrt{2}} p_y \quad (20.24)$$

The maximum value of these three eigenfunctions is readily found to be 1.991, in each case; this does not differ appreciably from that of the tetrahedral eigenfunction.

It is reasonable to expect, therefore, that under certain conditions *sp* hybridization will lead to the formation of three coplanar bonds at 120° . This is evidently the case with the trivalent compounds of boron, several of which have been shown, by dipole moment and electron diffraction measurements, to have planar configurations. In such compounds there are but six electrons in the outer shell of the boron atom, and hence the latter will readily accept a pair of electrons from an atom of oxygen, in ethers, or from nitrogen, in amines. In the resulting substances, the trigonal bond functions of the boron have probably become tetrahedral in character.

20e. Orbitals for Double Bonds.¹⁸—The concept of the overlapping of eigenfunctions as the basis of valence bonds encounters some difficulty if an attempt is made to utilize tetrahedral eigenfunctions in the formation of double bonds, e.g., between two carbon atoms. The properties of such bonds can, however, be readily accounted for by the use of the three trigonal (hybridized) wave functions of the type just considered. It may be supposed that when a carbon atom takes part in double bond formation, the one *s* and two *p* orbitals, i.e., p_x and p_y , combine to form three trigonal orbitals, whose maxima lead to the formation of three bonds, making angles of 120° with each other, lying in a plane, the *xy* plane. The fourth orbital, i.e., p_z , retains its *p* character unchanged, and so the fourth bond is oriented along the *z* axis, perpendicular to the plane containing the other three bonds. When two carbon atoms are joined by a double bond, it appears that one of the two linkages is formed by the overlapping of one trigonal eigenfunction from each atom, while the second linkage results from the pairing of two pure p_z orbitals. In normal (single) bonds, often referred to as $\sigma\sigma$ bonds, the maxima of the two orbitals involved lie on the same line, and this is the case with the first of the two linkages making up the double bond. The second linkage, involving the two pure p_z orbitals, is known as a $\pi\pi$ bond, and it is different in character; the two *p* orbitals are parallel to one another, as shown in Fig. 14. A double bond thus consists of one $\sigma\sigma$ and one $\pi\pi$ bond. These two linkages, as may be expected, have different strengths; this is evident from the fact that the energy required to break a $C=C$ bond is about 1.7 times as great as for a $C-C$ bond. It appears, therefore, that the strength of a $\pi\pi$ bond is about seven-tenths that of a $\sigma\sigma$ bond between carbon atoms.

The proposed structure of a double bond, as made up of a $\sigma\sigma$ and a $\pi\pi$ linkage, accounts for the absence of free rotation about bonds of this type.

¹⁸ Hückel, *Z. Physik*, 60, 423 (1930); Hund, *ibid.*, 73, 1 (1931); Pauling, refs. 11 and 16; Penney, *Proc. Roy. Soc., A*, 144, 166 (1934).

The symmetry of a $\sigma\sigma$ bond is such that rotation does not affect the extent of overlap of the eigenfunctions, and therefore the stability of the system; hence free rotation about a single bond is possible. With a $\pi\pi$ bond, however, the situation is different. The

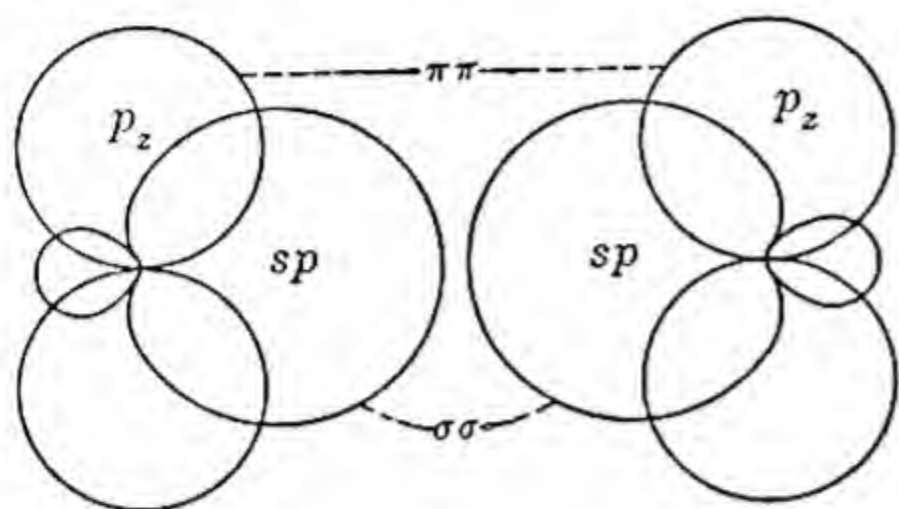


FIG. 14. Carbon-carbon double bond

two p_z orbitals will tend to overlap as much as possible, in order to give the maximum bond strength, and this will occur when they are parallel to one another and in the same plane. Any attempt to produce rotation about the double bond will cause the p_z orbitals to be twisted out of the plane, with the result that their overlapping is decreased. Such a procedure would

increase the potential energy of the system and would consequently require the supply of energy from outside. It is evident, therefore, that rotation about a double bond will be restricted in character.

According to the arguments presented at the beginning of this section, in a molecule, such as ethylene, which contains a double bond, one of the trigonal orbitals of each carbon atom is involved in the formation of the double bond, while the other two are available for $\sigma\sigma$ bond formation with hydrogen atoms. Since the trigonal orbitals of each carbon atom lie in a plane, and the two p_z orbitals are at right angles to this plane and parallel to each other, it follows that the four hydrogen atoms and the two carbon atoms of ethylene must lie in one plane. Further, all the bond angles in the plane should be 120° . There is evidence, however, that the angle between a single and a double bond in olefins is slightly greater than this value. It is possible that the carbon orbitals joined to hydrogen are largely tetrahedral in character; this will have the effect of reducing the angle between the two C—H bonds below 120° , while that between the C—H and C=C bonds will be increased correspondingly.

20f. Structure of Benzene and Graphite.—In benzene each carbon atom is joined to two other carbon atoms, one on each side, by means of the bonds involving trigonal orbitals; the third trigonal orbital of each carbon atom is concerned in the attachment of a hydrogen atom. This accounts for the planar configuration of benzene with all the bond angles equal to 120° . The p_z eigenfunction of each carbon atom is perpendicular to the plane of the ring; these six orbitals interact in pairs to form three $\pi\pi$ bonds. There is no unique method of pairing and, as will be seen later, it is because resonance occurs between the resulting different configurations that the benzene molecule has exceptional stability.

Reference may be made at this point to the difference between the structure of diamond and that of graphite. In the former, each carbon atom is attached to four others by bonds involving tetrahedral eigenfunctions, but in the latter, every carbon atom is joined to three others in the same plane by linkages derived from trigonal orbitals. The p_z orbitals of the carbon

atoms are perpendicular to the plane, and their overlapping to form π bonds, together with a resonance effect, is responsible for the stability of the carbon atom planes in graphite.

20g. Bond Eigenfunctions with d Orbitals.—With elements having electrons with principal quantum number equal to or greater than 3, there become available for bond formation d orbitals, in addition to s and p orbitals. Although the maximum value of a d orbital, e.g.,

$$d_z = \frac{1}{2}\sqrt{5}(3 \cos^2 \theta - 1), \quad (20.25)$$

is $\sqrt{5}$, i.e., 2.236, in this case when $\theta = 0^\circ$, hybridization with s and p orbitals, leads to bonds of still greater strength. By utilizing the methods previously described, Pauling has shown that one s , two p and one d orbitals can combine to give four equivalent bonding eigenfunctions with maxima, equal to 2.694, lying in one plane and directed at the corners of a square. The existence of this type of configuration has been established in the ions $\text{Ni}(\text{CN})_4^{--}$, PdCl_4^{--} and PtCl_4^{--} , as well as in many other coordination compounds of copper, nickel, palladium and gold. The element copper is of particular interest in this connection; bivalent copper can form either tetrahedral sp^3 bonds or the coplanar dsp^2 bonds considered here. It has been found, however, that the latter are generally preferred in the formation of four-coordinated compounds. It appears that the greater strength of the hybridized dsp^2 bonds (2.694), compared with that of the sp^3 bonds (2.00), is here the determining factor.

When two d orbitals are available for hybridization with s and p eigenfunctions, six equivalent orbitals, resulting from d^2sp^3 hybridization, with a maximum strength of 2.923, are possible. These six orbitals are directed towards the corners of a regular octahedron, and hence they account for this type of configuration, postulated by Werner and definitely established for a large number of six-coordinated compounds.

21a. Bond Orbitals and Bond Energies.¹⁹—Some indication of the relationship between the energy of a bond and the strength of the bond orbitals involved in its formation can be obtained by calculating the energies for one-electron bonds between two atoms. Assuming the eigenfunctions to be real, this energy is evaluated by means of the expression

$$E = \frac{\int \psi \mathbf{H} \psi d\tau}{\int \psi \psi d\tau}, \quad (21.1)$$

which is readily derived from the wave equation (6.9) by multiplying each side by ψ and integrating over the whole of the configuration space. The eigenfunctions ψ are assumed to be given by

$$\psi = c(\psi_A + \psi_B), \quad (21.2)$$

¹⁹ Pauling and Sherman, *J. Am. Chem. Soc.*, 59, 1450 (1937).

where ψ_A and ψ_B are similar hydrogen-like bond orbitals (Table IV), e.g., both $2s$ or both $2p$, of the atoms A and B; c is a normalization constant. The effective atomic number Z is taken to be unity in all cases. For a system consisting of one electron and two atomic nuclei, or two such nuclei together with completed electron shells, having a unit residual charge, the Hamiltonian operator is similar to that for the hydrogen molecule-ion; hence it is possible, by means of equation (21.1), to calculate the energy of the one-electron bond for various internuclear distances, r_{AB} , by evaluating the appropriate integrals. The results

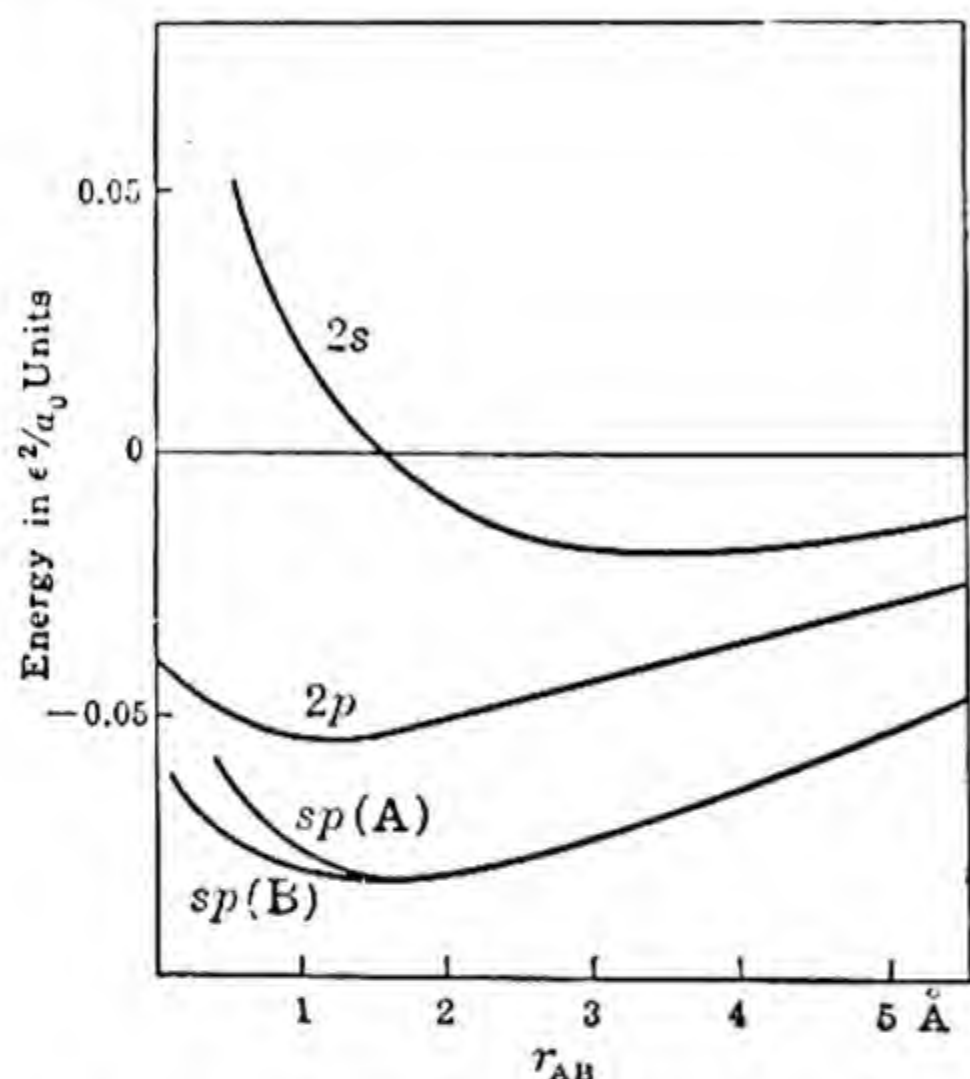


FIG. 15. Energies of one-electron bonds

obtained in this manner for $2s$ and $2p$ electrons are shown by the curves in Fig. 15. It is seen, in agreement with the conclusions reached previously, that the $2p$ orbitals form stronger bonds than do the $2s$ orbitals. Somewhat similar curves have been obtained for the energies of one-electron bonds involving $3s$ and $3p$ orbitals only.

It is of interest, now, to treat in an analogous manner one-electron bonds formed by sp hybridization. The atomic bond orbital is here assumed to be

$$\psi = a\psi_s + b\psi_p, \quad (21.3)$$

where ψ_s and ψ_p are not exactly the hydrogen-like eigenfunctions, but are modified, for simplicity, so that the radial parts, which are actually different, are taken as being identical. For hybridization between $2s$ and $2p$ orbitals, for example, the radial part of the eigenfunction is assumed to be equal to that for the $2p$ electron, i.e., $n = 2, l = 1$ is assumed in both cases. The complete eigenfunction is then obtained on multiplying by 1.0 for s , and by $\sqrt{3} \cos \theta$ for p . If the ratio of the coefficients b/a is taken as $\sqrt{3}$, which as seen in Section 20c corresponds to that for tetrahedral orbitals, the one-electron bond energy is represented as a function of internuclear distance by the curve marked $sp(A)$ in Fig. 15. An alternative calculation can be made by adjusting the ratio b/a for each value of r_{AB} in such a way as to minimize the energy integral; the results so obtained are indicated by the curve $sp(B)$. It is a very striking fact that over a considerable range of interatomic distances the tetrahedral sp orbitals actually provide the strongest bonding possible. In any case, the difference in energy between the tetrahedral bonds and the strongest feasible sp hybridized bonds is never large for reasonable internuclear distances. Quite analogous conclusions have been reached from calculations made for hybridization between $3s$ and $3p$ orbitals.

21b. Bond Energy and Orbital Strength.—The curves in Fig. 15 show, in agreement with the results obtained from the postulate concerning the overlapping of bond orbitals, that the s orbitals form the weakest bonds, the p orbitals yield somewhat stronger bonds and hybridized sp orbitals produce still stronger bonds. The bond energies represented by the minima of the $2s$, $2p$ and sp curves, indicating the maximum energies for one-electron bonds of these types, are seen to be 0.020, 0.054 and 0.082, respectively, in e^2/a_0 units. For the corresponding orbitals with principal quantum number 3, the maximum energies are 0.014, 0.037 and 0.057, respectively. It will be observed that in each case the three energies are approximately in the ratio of 1 : 3 : 4; these ratios are the squares of the strengths of the corresponding bond orbitals, namely 1 : $\sqrt{3}$: 2, previously calculated. It appears, therefore, that an expression such as

$$E = kS^2, \quad (21.4)$$

where k is a constant, relates the bond energy E to the strength S of the bond eigenfunction.

A test of this relationship has been obtained by calculating S for systems involving s and p electrons by means of the equation

$$S = \frac{a + b\sqrt{3}}{\sqrt{a^2 + b^2}}, \quad (21.5)$$

(see Section 20c), with the coefficient a varying from zero to 10, while b is equal to $10 - a$. With this normalization, S^2 increases from 3.0 for $a = 0$, i.e., for a pure p orbital, to a maximum of 4.0 for $a = 3.66$, i.e., for $b/a = 1.732$, which is the condition for a tetrahedral sp orbital, and then decreases to 1.0 for $a = 10$, i.e., for a pure s orbital. The complete results are shown by the dashed curve in Fig. 16. The corresponding bond energies for the various values of a and b have been calculated by means of equations (21.1) and (21.3), and these are plotted in the full curve in Fig. 16. The general agreement between the two sets of results is very definite, and provides confirmation of the view that the energy of a one-electron bond is related to the strength of the corresponding orbital.

An important corollary of the foregoing conclusion is that for bonds between two atoms with *unlike* orbitals ψ_A and ψ_B , the bond energy is given by the relationship

$$E = kS_A S_B, \quad (21.6)$$

where S_A and S_B are the strengths of the dissimilar bond orbitals. The energy of a bond formed between the eigenfunctions ψ_A and ψ_B , would thus be the geometric mean of the bond energies for ψ_A with ψ_A , which is proportional to S_A^2 , and for ψ_B with ψ_B , which is proportional to S_B^2 . This postulate is of importance in connection with the determination of the partial ionic character of covalent bonds. The difference between the observed energy E_{A-B} of the bond between atoms A and B, and the geometric mean of E_{A-A}

and E_{B-B} is taken as equal to the additional resonance energy due to the contribution of ionic structures to the eigenfunction of the system AB. This is the contribution of the ionic resonance energy described in Section 17c,

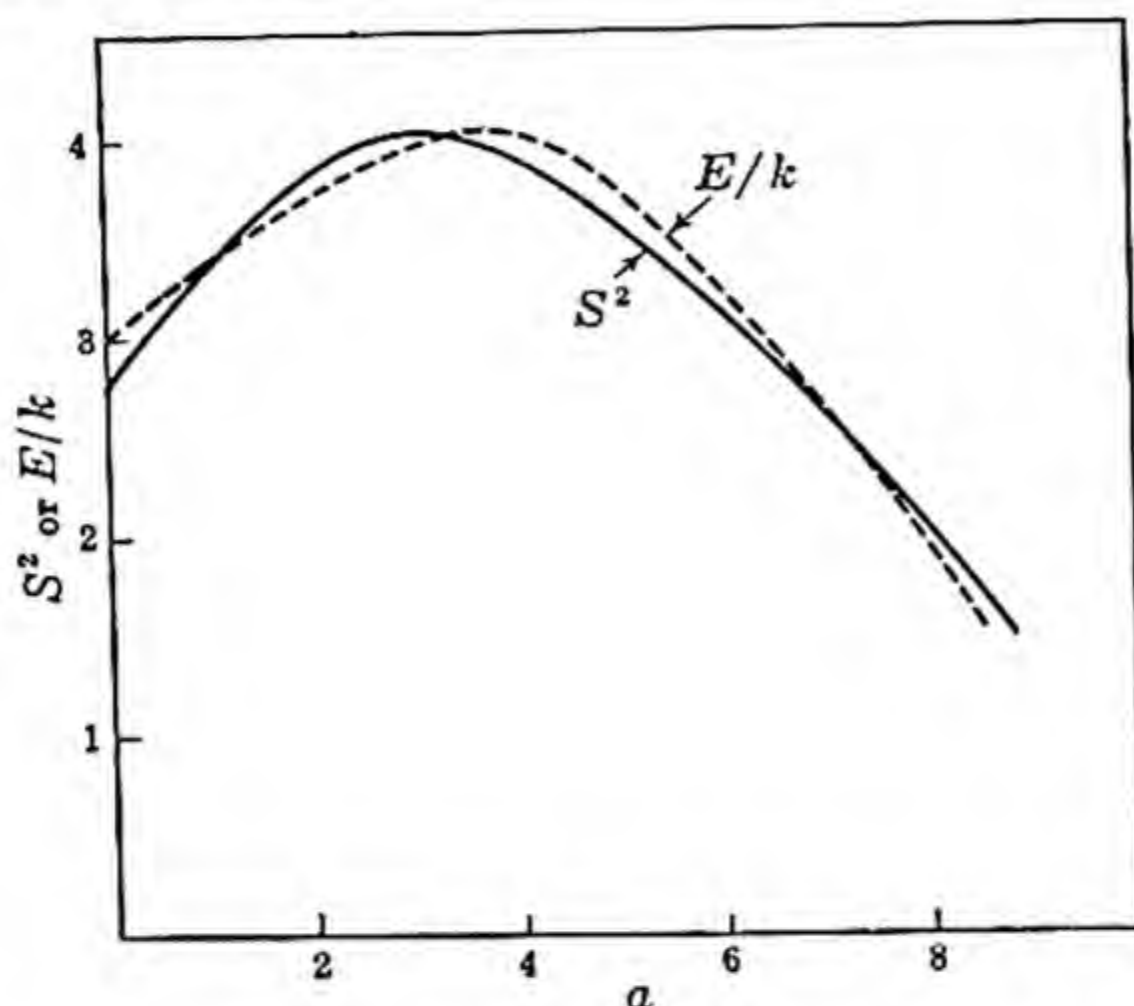


FIG. 16. Bond energies and orbital strengths

and which is regarded as a measure of the difference in electronegativity of the atoms A and B.

22. Quantitative Treatment of Localized Bond Orbitals.²⁰—The method of localized pairs (directed bond functions) can be considered from another point of view that is quantitative, at least in principle. However, because of its incompleteness it does not give in practice energy values that are in good agreement with experiment, although it leads to the expected conclusions with regard to molecular configurations and the formation of valence bonds. Before entering into the details of the treatment, reference must be made to a matter of nomenclature. It has been seen in Section 13h (footnote) that the three p orbitals at right angles are distinguished as $p\sigma$, $p\pi_+$ and $p\pi_-$; when the $p\sigma$ orbital lies along one of the axes x , y or z , this is indicated by the symbol $p\sigma_x$, $p\sigma_y$ or $p\sigma_z$, respectively.²¹ Because of the vector properties of the p eigenfunctions, it is possible to transform the $p\sigma_x$ orbital, referred to the x axis, into two orbitals $p\sigma$ and $p\pi$ referred to an axis making an angle θ with the x axis; thus

$$\psi_{p\sigma_x} = \psi_{p\sigma} \cos \theta + \psi_{p\pi} \sin \theta, \quad (22.1)$$

where $p\sigma$ lies along the new axis and $p\pi$ is in a direction perpendicular to it. This transformation will be employed in the ensuing discussion.

²⁰ Coolidge, *Phys. Rev.*, **42**, 189 (1932); Van Vleck and Cross, *J. Chem. Phys.*, **1**, 357 (1933); Hellmann, ref. 1; Penney, ref. 1; Van Vleck and Sherman, ref. 1.

²¹ For the significance of the symbols σ and π , see Section 40a.

In order to illustrate the method of treating localized bond orbitals, a relatively simple molecule, such as water, may be considered. The oxygen atom has, in addition to the two $2s$ electrons, which are not available for bond formation, three $2p$ orbitals, of which one, e.g., $p\sigma_z$, is already occupied by a pair of electrons with opposite spins, while the $p\sigma_x$ and $p\sigma_y$ orbitals, at right angles to each other, can take part in the formation of σ bonds. Suppose the three p orbitals of oxygen are represented by a , b and c in Fig. 17; c is the doubly occupied $p\sigma_z$ orbital, which is oriented in a direction perpendicular to the xy plane, i.e., the plane of the paper. The orbitals indicated by a and b are $p\sigma_x$ and $p\sigma_y$, respectively; these are perpendicular to one another, their maxima lying along the axes x and y , respectively, in the xy plane. The letters d and e refer to the $1s$ orbitals of two hydrogen atoms which combine with the oxygen atom to form a molecule of water. For convenience, d and e are placed symmetrically with regard to the x and y axes, so that the angle θ between the line ad and the x axis is equal to that between be and the y axis. That is to say, the two O—H bonds in the water molecule are arranged symmetrically with respect to the two axes. Utilizing equation (19.10), which gives an approximate estimate of the energy of a system in terms of the coulombic and exchange (resonance) integrals, it follows that for the present case

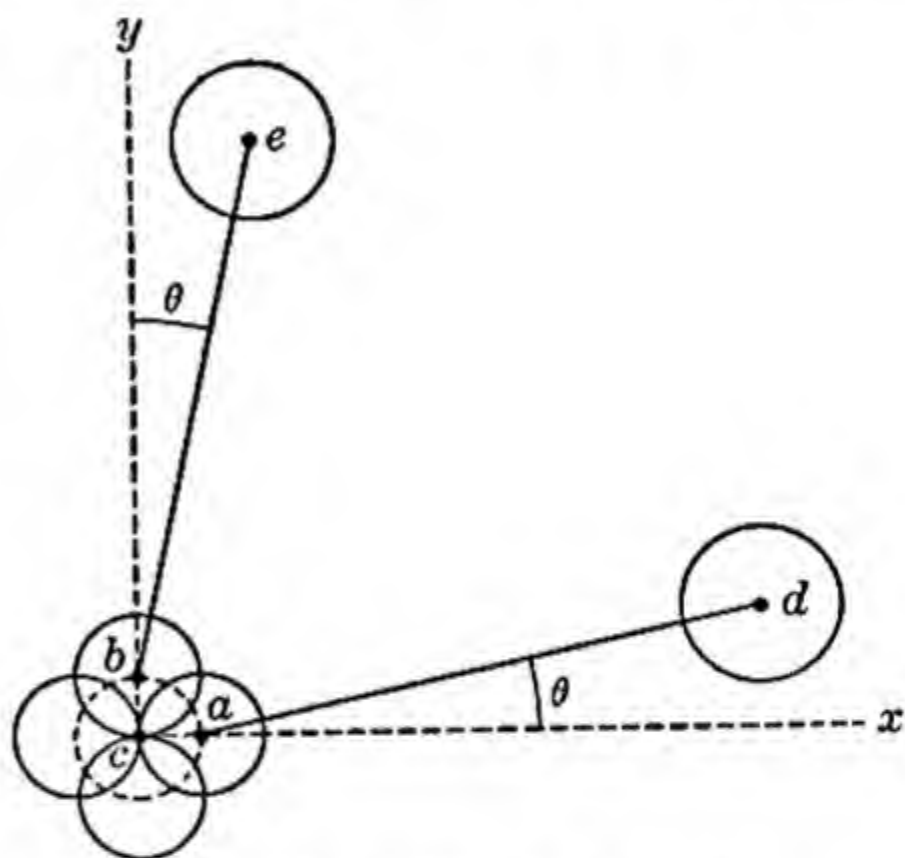


FIG. 17. Electron orbitals in water molecule

$$E_{\text{H}_2\text{O}} = Q + (ad) + (be) - \frac{1}{2}\{(ae) + (bd) + (de) + 2(cd) + 2(ce)\}, \quad (22.2)$$

where Q is the coulombic energy, and the symbols (ad) , etc., represent the exchange integrals for the interchange of the electrons a and d , etc. The terms (cd) and (ce) appear with the factor 2 because c represents two electrons.

The exchange integrals (ad) and (be) will be equal and these may be represented by

$$(ad) = (be) = \iint \psi_{p\sigma_x}(1)\psi_{\text{H}}(2)\mathbf{H}\psi_{p\sigma_x}(2)\psi_{\text{H}}(1)d\tau_1d\tau_2, \quad (22.3)$$

where ψ_{H} is the $1s$ orbital of a hydrogen atom; the two electrons involved in the bond formation are represented by (1) and (2), and \mathbf{H} is the interaction (Hamiltonian) operator, which is analogous to that given in equation (15.29). Resolving $\psi_{p\sigma_x}$ along two axes, one in the direction of and the other perpen-

dicular to the O—H bond, by means of equation (22.1), it follows that

$$(ad) = (be) = \int \int \{\psi_{p\sigma}(1) \cos \theta + \psi_{p\pi}(1) \sin \theta\} \psi_H(2) \\ \times H \{\psi_{p\sigma}(2) \cos \theta + \psi_{p\pi}(2) \sin \theta\} \psi_H(1) d\tau_1 d\tau_2. \quad (22.4)$$

Upon multiplying out and making use of the fact that integrals involving one σ and one π eigenfunction are always zero, e.g.,

$$\int \int \psi_{p\sigma}(1) \psi_H(2) H \psi_{p\pi}(2) \psi_H(1) d\tau_1 d\tau_2 = 0,$$

the result is

$$(ad) = (be) = \cos^2 \theta \int \int \psi_{p\sigma}(1) \psi_H(2) H \psi_{p\sigma}(2) \psi_H(1) d\tau_1 d\tau_2 \\ + \sin^2 \theta \int \int \psi_{p\pi}(1) \psi_H(2) H \psi_{p\pi}(2) \psi_H(1) d\tau_1 d\tau_2 \quad (22.5)$$

$$= N_{\sigma\sigma} \cos^2 \theta + N_{\pi\pi} \sin^2 \theta, \quad (22.6)$$

where the symbols $N_{\sigma\sigma}$ and $N_{\pi\pi}$ are used to represent the respective exchange integrals

$$N_{\sigma\sigma} = \int \int \psi_{p\sigma}(1) \psi_H(2) H \psi_{p\sigma}(2) \psi_H(1) d\tau_1 d\tau_2 \quad (22.7)$$

and

$$N_{\pi\pi} = \int \int \psi_{p\pi}(1) \psi_H(2) H \psi_{p\pi}(2) \psi_H(1) d\tau_1 d\tau_2. \quad (22.8)$$

In the same manner as just described, it can be shown, by making use of the transformation,

$$\psi_{p\sigma_v} = \psi_{p\sigma} \sin \theta + \psi_{p\pi} \cos \theta,$$

for the resolution of the $p\sigma_v$ orbital along the axis bd and perpendicular to it, that

$$(bd) = (ae) = \int \int \psi_{p\sigma_v}(1) \psi_H(2) H \psi_{p\sigma_v}(2) \psi_H(1) d\tau_1 d\tau_2 \quad (22.9)$$

$$= N_{\sigma\sigma} \sin^2 \theta + N_{\pi\pi} \cos^2 \theta. \quad (22.10)$$

The exchange integrals (cd) and (ce) can be written as

$$(cd) = (ce) = \int \int \psi_{p\sigma_z}(1) \psi_H(2) H \psi_{p\sigma_z}(2) \psi_H(1) d\tau_1 d\tau_2, \quad (22.11)$$

but as the $p\sigma_z$ orbital is perpendicular to the plane of the molecule, it follows that $\psi_{p\sigma_z}$ has no $p\sigma$ component in the xy plane, and so it is a pure $p\pi$ orbital.

The integral of equation (22.11) thus becomes

$$(cd) = (ce) = \int \int \psi_{pr}(1) \psi_H(2) H \psi_{pr}(2) \psi_H(1) d\tau_1 d\tau_2 \quad (22.12)$$

$$= N_{rr}. \quad (22.13)$$

Neglecting, for the present, the integral (de) , for exchange of electrons between the two hydrogen atoms, which are nonbonded, it follows that

$$\begin{aligned} E_{H_2O} &= Q + 2(N_{\sigma\sigma} \cos^2 \theta + N_{rr} \sin^2 \theta) \\ &\quad - (N_{\sigma\sigma} \sin^2 \theta + N_{rr} \cos^2 \theta) - 2N_{rr} \\ &= Q - 3(N_{\sigma\sigma} - N_{rr}) \sin^2 \theta + 2N_{\sigma\sigma} - 3N_{rr}. \end{aligned} \quad (22.14)$$

If the various integrals could be evaluated, this equation would provide a means for calculating the energy of a water molecule by means of quantum mechanics. Unfortunately, the results are not yet sufficiently accurate to have quantitative value, but a qualitative study of equation (22.14) is adequate to throw light on the problem of the oxygen valence angle.

It is to be expected, in a general way, that the exchange integral $N_{\sigma\sigma}$ will have a large negative value, that is, it will lead to attraction as in the case of the hydrogen molecule. On the other hand, the exchange integral N_{rr} is probably small numerically, and this has been confirmed by actual evaluation of the integral, using appropriate $p\pi$ orbital wave functions.²² It follows, therefore, that if E_{H_2O} is to have as large a negative value as possible, i.e., for maximum stability of the water molecule, the quantity $(N_{\sigma\sigma} - N_{rr}) \sin^2 \theta$ should have the largest possible positive value. Since $N_{\sigma\sigma} - N_{rr}$ is negative, as seen above, it is evident that $\sin^2 \theta$ must be zero, if $(N_{\sigma\sigma} - N_{rr}) \sin^2 \theta$ is not to be negative. In other words, the most stable form of the water molecule will be that in which the angle θ is zero. The angle between the two O—H bonds in water should thus be 90° . This is exactly the result that was obtained previously on the basis of the postulate that the direction of a valence bond is that in which the orbital functions of the electrons overlap as much as possible. The foregoing treatment of the water molecule may be regarded as a substantiation of this postulate.

It will be recalled that in the derivation of equation (22.14) the exchange integral (de) was neglected; it is known, however, from the hydrogen molecule problem, that this resonance energy is quite appreciable, and consequently it is likely to have an influence on the bond angle. The integral (de) appears as a negative term in equation (22.2), and since (de) is itself negative, it should be small, numerically, in order to permit maximum stability of the water molecule. That is to say, the tendency will be for the two hydrogen atoms to be as far apart as possible. The effect of the exchange integral (de) will thus be to increase the bond angle in water to a value in excess of 90° . By making the assumption that the resonance energy

²² Coolidge, ref. 20; see also, Van Vleck and Cross, ref. 20; Van Vleck, *J. Chem. Phys.*, 2, 20 (1934); Penney, *Trans. Faraday Soc.*, 31, 734 (1935).

constitutes 0.88 of the total binding energy of a hydrogen molecule (cf. Section 17b), utilizing a Morse function (Section 32b) to give the variation of this energy with the distance between the hydrogen atoms, and introducing calculated values of $N_{\sigma\sigma}$ and $N_{\tau\tau}$, it is found that θ should be about 5° in order to minimize the energy of the water molecule. This would make the angle between the O—H bonds in water equal to 100° , as compared with the experimental value of 105° .

MOLECULAR ORBITALS AND VALENCE

23. Molecular Orbitals and Molecular Configuration.²³—Although the concept of molecular orbitals does not involve the occurrence of localized electron pairs which represent valence bonds, it is of interest to note that the treatment leads to the expectation that certain molecular configurations are the most stable. In the particular cases of the molecules of water and methane, the lowest energy states are found to have spatial arrangements similar to those derived by the method of directed valence bonds; the bond angles are calculated to be 90° and $109^\circ 28'$, respectively. The procedure adopted in the determination of the best configuration may be illustrated, again, by consideration of the water molecule. Disregarding the two $2s$ electrons, which have central symmetry, and the two electrons occupying the $2p\sigma_z$ orbital, which in any case exerts no directional effect since its axis is perpendicular to the plane of the water molecule, there remain four orbitals to be considered. These are ψ_{H_a} and ψ_{H_b} , the two $1s$ orbitals of the two hydrogen atoms H_a and H_b , respectively, and ψ_{p_x} and ψ_{p_y} , the two $2p$ orbitals of the oxygen atom. It is convenient to take in place of these four atomic orbitals, the following eigenfunctions, which are linear combinations of the atomic orbitals, viz.,

$$\psi_1 = \frac{1}{\sqrt{2}} (\psi_{H_a} + \psi_{H_b}), \quad \psi_2 = \frac{1}{\sqrt{2}} (\psi_{H_a} - \psi_{H_b}), \quad (23.1)$$

$$\psi_3 = \frac{1}{\sqrt{2}} (\psi_{p_x} + \psi_{p_y}) \quad \text{and} \quad \psi_4 = \frac{1}{\sqrt{2}} (\psi_{p_x} - \psi_{p_y}), \quad (23.2)$$

where the factor $1/\sqrt{2}$ is introduced for normalization purposes. This change in the eigenfunctions leads to a considerable simplification in the secular equation for the problem under examination. According to the fundamental basis of the molecular orbital treatment (Section 16b), the wave function for each electron may be expressed as a linear combination of the four atomic orbitals, ψ_1 , ψ_2 , ψ_3 and ψ_4 , and hence by the variation theorem, the appropriate secular equation is

$$\begin{vmatrix} H_{11} - \Delta_{11}E & H_{12} - \Delta_{12}E & H_{13} - \Delta_{13}E & H_{14} - \Delta_{14}E \\ H_{21} - \Delta_{21}E & H_{22} - \Delta_{22}E & H_{23} - \Delta_{23}E & H_{24} - \Delta_{24}E \\ H_{31} - \Delta_{31}E & H_{32} - \Delta_{32}E & H_{33} - \Delta_{33}E & H_{34} - \Delta_{34}E \\ H_{41} - \Delta_{41}E & H_{42} - \Delta_{42}E & H_{43} - \Delta_{43}E & H_{44} - \Delta_{44}E \end{vmatrix} = 0. \quad (23.3)$$

²³ Hund, *Z. Physik*, 73, 1, 565 (1931); 74, 429 (1932); Van Vleck, *J. Chem. Phys.*, 1, 177, 219 (1933); Van Vleck and Sherman, ref. 1.

The orientations of the x and y axes can be chosen arbitrarily without loss of generality, and if these are arranged, as in Fig. 17, so as to be symmetrical with respect to the O—H bonds²⁴ of the water molecule, it is found that the matrix elements H_{13} , H_{14} , H_{23} , H_{24} , H_{31} , H_{41} , H_{32} and H_{42} are all zero. The reason for this is to be found in the realization that the eigenfunctions ψ_1 and ψ_2 are "even," as also is the Hamiltonian operator, whereas ψ_3 and ψ_4 are "odd," in the sense described in Sections 2e and 31b. If the integrand as a whole is odd, that is, if it contains one or three odd factors, it will be zero; thus

$$H_{13} = \int \psi_1 \mathbf{H} \psi_3 d\tau = 0.$$

On the other hand, integrals involving two odd terms, such as H_{34} and H_{43} , are not zero. If the eigenfunctions ψ_1 , ψ_2 , ψ_3 and ψ_4 are supposed to be normalized and orthogonal, so that Δ_{ij} is equal to unity when $i = j$, or to zero when $i \neq j$, the secular equation (23.3) reduces to

$$\begin{vmatrix} H_{11} - E & H_{12} & 0 & 0 \\ H_{21} & H_{22} - E & 0 & 0 \\ 0 & 0 & H_{33} - E & H_{34} \\ 0 & 0 & H_{43} & H_{44} - E \end{vmatrix} = 0. \quad (23.4)$$

This equation can immediately be factorized into two second order equations of the form

$$\begin{vmatrix} H_{11} - E & H_{12} \\ H_{21} & H_{22} - E \end{vmatrix} = 0. \quad (23.5)$$

Because of certain (Hermitian) properties of the Hamiltonian operator, H_{12} is equal to H_{21} , and H_{34} is equal to H_{43} ; the lowest root of equation (23.5) is then

$$E' = \frac{1}{2}[(H_{11} + H_{22}) - \{(H_{11} - H_{22})^2 + 4H_{12}^2\}^{1/2}], \quad (23.6)$$

while that of the other equation, analogous to (23.5) is

$$E'' = \frac{1}{2}[(H_{33} + H_{44}) - \{(H_{33} - H_{44})^2 + 4H_{34}^2\}^{1/2}]. \quad (23.7)$$

The total energy E of the system of four electrons is obtained by taking the sum of twice each of these energy values, i.e.,

$$E = 2E' + 2E'', \quad (23.8)$$

but before proceeding to make this summation, some simplification is possible. The coulombic integrals, represented by the matrix components H_{11} and H_{33} , refer to the energy of the single electrons on the two hydrogen atoms, and hence they are not only equal, but are also independent of the spatial configuration of the water molecule. These integrals may thus be replaced

²⁴ The term "bond" as used in the molecular orbital treatment refers to the line joining the nuclei of the atoms concerned, e.g., oxygen and hydrogen in the present instance.

by the symbol E_H . The same considerations apply to H_{22} and H_{44} which refer to single electrons on the oxygen atom, and for these the symbol E_O may be employed. It follows, therefore, from equations (23.6), (23.7) and (23.8), that

$$E = 2E_H + 2E_O - \{(E_H - E_O)^2 + 4H_{12}^2\}^{1/2} - \{(E_H - E_O)^2 + 4H_{34}^2\}^{1/2}. \quad (23.9)$$

Since E_H and E_O have no angular dependence, the angular structure of the water molecule must depend on the exchange integrals H_{12} and H_{34} , defined by

$$H_{12} = \int \psi_1 \mathbf{H} \psi_2 d\tau = \frac{1}{2} \int (\psi_{H_a} + \psi_{H_b}) \mathbf{H} (\psi_{p\sigma_x} + \psi_{p\sigma_y}) d\tau, \quad (23.10)$$

and

$$H_{34} = \int \psi_3 \mathbf{H} \psi_4 d\tau = \frac{1}{2} \int (\psi_{H_a} - \psi_{H_b}) \mathbf{H} (\psi_{p\sigma_x} - \psi_{p\sigma_y}) d\tau. \quad (23.11)$$

Because of the transformation properties of the $2p$ orbitals [cf. equation (22.1)], it is possible to write

$$\psi_{p\sigma_x} = \psi_{p\sigma} \cos \theta + \psi_{p\tau} \sin \theta \quad (23.12)$$

for resolution along the line of the O—H bond, and perpendicular to it; θ is the angle between the x axis and the O—H bond (cf. Fig. 17). Similarly, the components of $\psi_{p\sigma_y}$ in the same two directions are given by

$$\psi_{p\sigma_y} = \psi_{p\sigma} \sin \theta + \psi_{p\tau} \cos \theta. \quad (23.13)$$

Noting that ψ_{H_a} and ψ_{H_b} are $1s$, and hence σ , orbitals, and remembering that integrals involving one σ and one π eigenfunction are zero, it follows from equations (23.10), (23.11), (23.12) and (23.13), that

$$H_{12} = \int (\psi_{H_a} + \psi_{H_b}) \mathbf{H} \psi_{p\sigma_a} (\cos \theta + \sin \theta) d\tau \quad (23.14)$$

and

$$H_{34} = \int (\psi_{H_a} - \psi_{H_b}) \mathbf{H} \psi_{p\sigma_b} (\cos \theta - \sin \theta) d\tau, \quad (23.15)$$

where the suffixes a and b as applied to $p\sigma$ refer to resolution along the O—H_a and O—H_b directions, respectively.

It can be seen that equation (23.9) for the energy involves the terms H_{12} and H_{34} , and consequently the angular dependence of E is determined by the quantities $(\cos \theta + \sin \theta)$ and $(\cos \theta - \sin \theta)$ which occur in the expressions for H_{12} and H_{34} , respectively. It is apparent that these quantities are unchanged when θ is replaced by $\frac{1}{2}\pi - \theta$, and hence it follows that E will have its extreme values, maxima and minima, when θ is $0, \frac{1}{4}\pi, \frac{1}{2}\pi, \frac{3}{4}\pi$, etc. Of these values $\theta = 0, \frac{1}{2}\pi$, etc., evidently correspond to minima of equation

(23.9), because of the negative signs. If θ is zero, the angle between the lines joining the oxygen nucleus with the two hydrogen nuclei is 90° , and the same will be true if θ is $\frac{1}{2}\pi$, π , etc. In other words, the molecular orbital treatment, although it does not involve the postulate of localized electron pairs, leads to a structure for the water molecule identical with that derived by the method of directed valence bonds. In the foregoing calculation no allowance was made for the interaction of the electrons in the two hydrogen atoms; if this were introduced, it would have the effect of increasing the angle between the O—H_a and O—H_b directions.

SYSTEMS OF SEVERAL ELECTRONS

24a. Antisymmetric Eigenfunctions.—The method described in Section 19d for calculating the energy of a system of several electrons is not really complete because it does not take into account the possibility of resonance among various configurations. An improved, although by no means perfect, procedure for evaluating the energy will be considered here, and some of its applications will then be described. The first problem is to derive a suitable eigenfunction for the system of a number of electrons, and Slater's extension of the Heitler-London method is very convenient.²⁵ Suppose there are n electrons, represented by the numerals 1, 2, 3, \dots , n , and an equal number of single electron orbital eigenfunctions a, b, c, \dots, n ; each of these orbital functions will be associated with a spin eigenfunction, α or β , to complete the wave function of the electron. Consider a perfectly general case in which the available eigenfunctions are, for example, $a\alpha, b\beta, c\beta, \dots, n\alpha$; let electron 1 occupy the orbital a , while electron 2 occupies b , electron 3 occupies c , and so on. A possible eigenfunction for the whole system would then be obtained, as in the Heitler-London treatment, by multiplying together the single electron wave functions; thus,

$$\psi = (a\alpha)_1(b\beta)_2(c\beta)_3 \cdots (n\alpha)_n, \quad (24.1)$$

where the subscript numerals indicate which electron occupies each particular orbital. Since the energy of the system would be unchanged if the coordinates of any pair of electrons, say 1 and 3, were interchanged, an equally satisfactory eigenfunction would be

$$\psi = (a\alpha)_3(b\beta)_2(c\beta)_1 \cdots (n\alpha)_n. \quad (24.2)$$

Other interchanges lead to equivalent eigenfunctions, and so it is possible to write a general expression for the eigenfunction of the system, viz.,

$$\psi = \mathbf{P}(a\alpha)_1(b\beta)_2(c\beta)_3 \cdots (n\alpha)_n, \quad (24.3)$$

where \mathbf{P} stands for the permutation operator which represents the operation of exchanging the coordinates of, that is, the orbitals occupied by, any pair of electrons. So far no consideration has been given to the question of

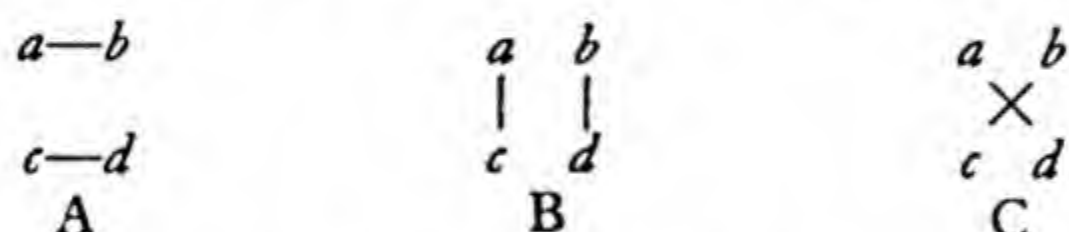
²⁵ Slater, *Phys. Rev.*, 38, 1109 (1931).

opposite spins; if the number of electrons is odd, there will be one electron over, when all the others have coupled. Consider a system of four electrons with four available orbitals, a , b , c and d ; for a stable system, two of the electrons will thus have α spin functions and the other two will have β spin functions. Six arrangements are then possible, as follows:

	a	b	c	d	Eigenfunction
I	α	β	α	β	ψ_I
II	α	α	β	β	ψ_{II}
III	α	β	β	α	ψ_{III}
IV	β	α	α	β	ψ_{IV}
V	β	α	β	α	ψ_V
VI	β	β	α	α	ψ_{VI}

The corresponding antisymmetrical eigenfunctions are designated by the symbols ψ_I , ψ_{II} , ψ_{III} , ψ_{IV} , ψ_V and ψ_{VI} . Each of these functions would be a satisfactory solution for the problem, as also would be a linear combination of them. By postulating the pairing of electrons, the number of suitable eigenfunctions has thus been reduced from sixteen to six.

As mentioned above, a further simplification is now possible by the use of bond eigenfunctions; these are based on the possible ways of pairing the available electrons. In the four-electron system there must be two bonds, of course, and these may be arranged in three ways; thus,



which may be represented by the letters A, B and C. Consider, first, the configuration A; each bond means that the pair of electrons involved in the bond, viz., a and b , and c and d , have opposite spins. This requirement is satisfied only by the arrangements I, III, IV and V given above, and hence only ψ_I , ψ_{III} , ψ_{IV} and ψ_V will appear in the bond eigenfunction of the configuration A. The bond eigenfunction is now obtained by forming a linear combination of the antisymmetric functions ψ_I , ψ_{III} , ψ_{IV} and ψ_V ; taking ψ_I as positive, the sign is changed for each interchange in the order of α and β that is necessary to convert ψ_I into the other functions. Thus, ψ_{III} is negative (one interchange), ψ_{IV} is negative (one interchange), and ψ_V is positive (two interchanges). The bond eigenfunction for the structure A is thus

$$\psi_A = \frac{1}{\sqrt{4}} (\psi_I - \psi_{III} - \psi_{IV} + \psi_V), \quad (24.6)$$

where $1/\sqrt{4}$ is the approximate normalization factor. In exactly the same

manner the bond eigenfunction for configuration B is found to be

$$\psi_B = \frac{1}{\sqrt{4}} (\psi_{II} - \psi_{III} - \psi_{IV} + \psi_{VI}), \quad (24.7)$$

while that for structure C is

$$\psi_C = \frac{1}{\sqrt{4}} (\psi_I - \psi_{II} + \psi_V - \psi_{VI}). \quad (24.8)$$

The three bond eigenfunctions, represented by equations (24.6), (24.7) and (24.8) are, however, not independent, since $\psi_C = \psi_A - \psi_B$. The system C, with crossed bonds, can thus be expressed in terms of the systems with uncrossed bonds; this result is an illustration of a completely general rule: any simple crossed bond can be described in terms of two uncrossed bonds. Structures with nonintersecting bonds are independent, and they are referred to as *canonical structures*; any possible arrangement of the electrons in the form of bonds can be represented in terms of the complete set of such structures, known as the *canonical set*.

24c. The Four-Electron Problem.—The use of bond eigenfunctions has permitted the reduction of the four-electron problem to the state when there are but two, instead of sixteen, independent eigenfunctions, viz., ψ_A and ψ_B , for the system. The variation function may be taken as a linear combination of these (real) eigenfunctions, and the secular equation for the problem is consequently the second order determinant

$$\begin{vmatrix} H_{AA} - \Delta_{AA}E & H_{AB} - \Delta_{AB}E \\ H_{BA} - \Delta_{BA}E & H_{BB} - \Delta_{BB}E \end{vmatrix} = 0, \quad (24.9)$$

where

$$H_{AA} = \int \psi_A \mathbf{H} \psi_A d\tau, \quad H_{BB} = \int \psi_B \mathbf{H} \psi_B d\tau$$

(24.10)

and

$$H_{AB} = H_{BA} = \int \psi_A \mathbf{H} \psi_B d\tau,$$

$$\Delta_{AA} = \int \psi_A \psi_A d\tau, \quad \Delta_{BB} = \int \psi_B \psi_B d\tau$$

(24.11)

and

$$\Delta_{AB} = \Delta_{BA} = \int \psi_A \psi_B d\tau.$$

If the eigenfunctions ψ_A and ψ_B are known, it should be possible to solve the quadratic equation represented by (24.9) and so evaluate the energy of the four-electron system. These eigenfunctions can be expressed in terms of $\psi_I, \psi_{II}, \dots, \psi_{VI}$ by equations (24.6) and (24.7), and hence it is possible to write H_{AA}, Δ_{AA} , etc., in terms of the corresponding matrix elements of the latter eigenfunctions. Since each $\psi_I, \psi_{II}, \dots, \psi_{VI}$ involves a fourth order de-

terminant, the result would appear to be very cumbersome, but considerable simplification follows appropriate consideration of the spin eigenfunctions.

24d. Nondiagonal Matrix Elements.—Consider the integral $H_{I II}$, defined by

$$H_{I II} = \int \psi_I \mathbf{H} \psi_{II} d\tau, \quad (24.12)$$

where the antisymmetric eigenfunctions ψ_I and ψ_{II} can be written as [cf. equation (24.4)]

$$\psi_I = \frac{1}{\sqrt{4!}} \sum \pm \mathbf{P}_I (a\alpha)_1 (b\beta)_2 (c\alpha)_3 (d\beta)_4 \quad (24.13)$$

and

$$\psi_{II} = \frac{1}{\sqrt{4!}} \sum \pm \mathbf{P}_{II} (a\alpha)_1 (b\alpha)_2 (c\beta)_3 (d\beta)_4, \quad (24.14)$$

in which \mathbf{P}_I and \mathbf{P}_{II} represent the permutation operators. It follows, therefore, that

$$H_{I II} = \frac{1}{4!} \int \sum \pm \mathbf{P}_I (a\alpha)_1 (b\beta)_2 (c\alpha)_3 (d\beta)_4 \times \mathbf{H} \{ \sum \pm \mathbf{P}_{II} (a\alpha)_1 (b\alpha)_2 (c\beta)_3 (d\beta)_4 \} d\tau. \quad (24.15)$$

Since the permutations include every possible exchange of the coordinates of pairs of electrons, as explained above, the result will be unchanged if the integrand in (24.15) is multiplied throughout by any other permutation operator \mathbf{P} . If the latter is chosen successively in such a way as to reverse each operation \mathbf{P}_I in the summation, i.e., $\mathbf{P} = \mathbf{P}_I^{-1}$, so that $\mathbf{P}\mathbf{P}_I$ is the *identity operator* that leaves the original arrangement unchanged, then every term in the summation involved in ψ_I will be the same. It follows, therefore, that

$$\sum \pm \mathbf{P}\mathbf{P}_I (a\alpha)_1 (b\beta)_2 (c\alpha)_3 (d\beta)_4 = 4! \{ (a\alpha)_1 (b\beta)_2 (c\alpha)_3 (d\beta)_4 \}, \quad (24.16)$$

since there are $4!$ terms in the summation. The expression for $H_{I II}$ thus becomes

$$H_{I II} = \int \{ (a\alpha)_1 (b\beta)_2 (c\alpha)_3 (d\beta)_4 \} \mathbf{H} \{ \sum \pm \mathbf{P}' (a\alpha)_1 (b\alpha)_2 (c\beta)_3 (d\beta)_4 \} d\tau, \quad (24.17)$$

where the operator \mathbf{P}' replaces $\mathbf{P}\mathbf{P}_{II}$. It will be noted that the factor $1/4!$ in equation (24.15) cancels out with $4!$ in equation (24.16); this is not entirely a matter of chance, for the normalization factor $1/\sqrt{4!}$ in the eigenfunctions was chosen partly with this end in view.

A further reduction in the integral $H_{I II}$ can be achieved by making use of the assumption (Section 19a) that orbital and spin portions of the eigenfunction do not interact. The integral in equation (24.17) contains $4!$, i.e., 24, terms, because of the permutations implied by the operator \mathbf{P}' ; one of

these terms, chosen at random, and to which the symbol I may be given, is

$$I = \int \{(a\alpha)_1(b\beta)_2(c\alpha)_3(d\beta)_4\} \mathbf{H} \{(a\alpha)_2(b\alpha)_3(c\beta)_1(d\beta)_4\} d\tau. \quad (24.18)$$

If the Hamiltonian does not operate on the spin functions, as indicated above, the orbital and spin parts in the integral may be separated; thus,

$$I = \int (a_1 b_2 c_3 d_4) \mathbf{H} (a_2 b_3 c_1 d_4) d\tau \int \alpha_1 \beta_1 d\omega \int \alpha_2 \beta_2 d\omega \int \alpha_3^2 d\omega \int \beta_4^2 d\omega, \quad (24.19)$$

where $d\omega$ is an element of spin space. The spin eigenfunctions are always supposed to be normalized and mutually orthogonal, so that

$$\begin{aligned} \int \alpha_1 \beta_1 d\omega &= 0, & \int \alpha_2 \beta_2 d\omega &= 0, \\ \int \alpha_3^2 d\omega &= 1 & \text{and} & \int \beta_4^2 d\omega = 1. \end{aligned} \quad (24.20)$$

It follows, therefore, that the integral I given in equation (24.18) must be zero. It can be seen that all other analogous integrals will be zero *unless the spin eigenfunctions before and after the Hamiltonian operator match exactly*; in the latter case all the spin terms similar to those in equations (24.20) will be unity. The matrix components of the operator \mathbf{H} , such as $H_{\text{I I}}$, $H_{\text{I II}}$, etc., that are not zero will consequently be equal to the orbital functions only, the integrals of the spin function being unity. In the case of the matrix element $H_{\text{I II}}$, defined by equation (24.17), there are only four terms that are not zero; these are:

$$\begin{aligned} \text{(i)} & \quad - \int \{(a\alpha)_1(b\beta)_2(c\alpha)_3(d\beta)_4\} \mathbf{H} \{(a\alpha)_1(b\alpha)_3(c\beta)_2(d\beta)_4\} d\tau \\ \text{(ii)} & \quad + \int \{(a\alpha)_1(b\beta)_2(c\alpha)_3(d\beta)_4\} \mathbf{H} \{(a\alpha)_3(b\alpha)_1(c\beta)_2(d\beta)_4\} d\tau \\ \text{(iii)} & \quad + \int \{(a\alpha)_1(b\beta)_2(c\alpha)_3(d\beta)_4\} \mathbf{H} \{(a\alpha)_1(b\alpha)_3(c\beta)_4(d\beta)_2\} d\tau \\ \text{(iv)} & \quad - \int \{(a\alpha)_1(b\beta)_2(c\alpha)_3(d\beta)_4\} \mathbf{H} \{(a\alpha)_3(b\alpha)_1(c\beta)_4(d\beta)_2\} d\tau. \end{aligned}$$

The signs preceding the integrals are determined in accordance with the significance of the operator $\pm \mathbf{P}'$, namely, a positive sign when the number of permutations from the initial state is even, and a negative sign for an odd number of permutations. The integral in (i) arises from the single exchange of the orbitals b and c in the original form $(a\alpha)_1(b\alpha)_2(c\beta)_3(d\beta)_4$, of ψ_{II} (equation (24.14)); hence its sign is negative. Integrals (ii) and (iii) both result from two permutations, viz., $a-b$ and $a-c$ in (ii) and $c-d$ and $b-d$ in (iii);

hence these have positive signs. Finally, the integral (iv) arises from three exchanges in the initial form of ψ_{II} , viz., $a-b$, $c-d$ and $a-d$, so that the sign of this integral is negative.

It can be shown that if the orbital functions were mutually orthogonal, the integrals resulting from the exchange of more than one pair of electrons would be zero. In practice, however, these eigenfunctions are not completely orthogonal; nevertheless, the departure from orthogonality is not large, and the integrals that involve more than one permutation, the so-called *multiple-exchange integrals*, may be taken as virtually zero. It follows, therefore, that of the four integrals given above, integral (i), which is a *single-exchange integral*, is the only one different from zero. This means that all the integrals involved in $H_{I II}$, except the resonance integral (i), are zero for one reason or another; hence $H_{I II}$ is equal to integral (i), and since the spin contribution of the latter is unity, as already seen, it follows that

$$H_{I II} = - \int (a_1 b_2 c_3 d_4) \mathbf{H} (a_1 b_3 c_2 d_4) d\tau.$$

This result is frequently abbreviated by omitting the numerals and writing the orbitals in the order of the subscripts; at the same time the integration is indicated by two vertical lines; thus

$$H_{I II} = - (abcd | H | acbd) = - (bc). \quad (24.21)$$

A still further simplification is achieved by writing this integral merely as $-(bc)$, which implies a single-exchange (resonance) integral involving a permutation of the coordinates of the orbitals b and c .

The important achievement represented by the foregoing arguments is that the complex expression of equation (24.15) has been reduced to the single term of equation (24.21). The general rule for carrying out this simplification is as follows: The matrix component H_{ij} between two *different* antisymmetric (determinantal) eigenfunctions is zero unless the two eigenfunctions differ only by a single interchange of spins in two orbitals; in the latter case, it is equal to the negative of the single exchange (resonance) integral between these orbitals. Consideration of the six arrangements in Section 24b shows that I and II differ only by the interchange of the spins on the orbitals b and c ; hence the general rule leads to the result obtained above. Similarly, for some other cases, it is found that

$$\begin{aligned} H_{I III} &= - (abcd | H | abdc) = - (cd) \\ H_{I IV} &= - (abcd | H | bacd) = - (ab) \\ H_{III IV} &= - (abcd | H | bacd) = - (ab) \\ H_{IV V} &= - (abcd | H | abdc) = - (cd). \end{aligned} \quad (24.22)$$

These matrix components are required for later use. Among others, mention may be made of the elements $H_{I IV}$ and $H_{IV IV}$; these are both zero, since they each involve the two exchanges a and b , and c and d .

24e. Diagonal Matrix Elements.—Attention must now be turned to the diagonal matrix elements, that is, the ones involving two identical eigenfunctions, e.g., $H_{II I}$, $H_{III III}$, etc.; these can be simplified in a manner exactly similar to that already described for the nondiagonal matrix element $H_{I II}$. It is found, for example, that

$$H_{II I} = (abcd|H|abcd) - (abcd|H|cbad) - (abcd|H|adcb). \quad (24.23)$$

The first integral, which is the matrix component of the Hamiltonian operator between two identical orbital eigenfunctions, is the coulombic integral; this is given the symbol Q and has the same significance as described in Section 15c, except that two (or more) electron pairs are now concerned. The expression (24.23) for $H_{II I}$ may thus be written as

$$H_{II I} = Q - (ac) - (bd). \quad (24.24)$$

The general rule for evaluating the diagonal matrix component is to take the coulombic integral and subtract all exchange (resonance) integrals between orbitals associated with the same spin. It is seen that in configuration I (p. 117) the two orbitals a and c have the same spin, as also do the orbitals b and d ; the result in equation (24.24) then follows directly from the rule. Some of the other diagonal elements, which will be required shortly, are readily found to be given by

$$\begin{aligned} H_{III III} &= (abcd|H|abcd) - (abcd|H|dbca) - (abcd|H|acbd) \\ &= Q - (ad) - (bc) \\ H_{IV IV} &= (abcd|H|abcd) - (abcd|H|dbca) - (abcd|H|acbd) \\ &= Q - (ad) - (bc) \\ H_{VV V} &= (abcd|H|abcd) - (abcd|H|cbad) - (abcd|H|adcb) \\ &= Q - (ac) - (bd). \end{aligned} \quad (24.25)$$

It is now possible to proceed to the evaluation of the integrals H_{AA} , H_{AB} and H_{BB} required for the solution of the secular equation (24.9). Utilizing the expression for ψ_A in equation (24.6), it is seen that

$$\begin{aligned} H_{AA} &= \int \psi_A \mathbf{H} \psi_A d\tau \\ &= \frac{1}{4} \{ (H_{II I} + H_{III III} + H_{IV IV} + H_{VV V}) \\ &\quad - 2(H_{I III} + H_{I IV} + H_{III V} + H_{IV V} - H_{I V} - H_{III IV}) \}. \end{aligned} \quad (24.26)$$

Introducing the values for the matrix components, given by equations (24.21), (24.22), (24.24) and (24.25), the result is

$$\begin{aligned} H_{AA} &= \frac{1}{4} \{ 4Q - 2(ac) - 2(bd) - 2(ad) - 2(bc) + 4(ab) + 4(cd) \} \\ &= Q - \frac{1}{2} \{ (ac) + (bd) + (ad) + (bc) \} + (ab) + (cd). \end{aligned} \quad (24.27)$$

24f. General Rules.²⁶—The other integrals in equation (24.9) can be obtained in an analogous manner, but there are certain general rules which

²⁶ Eyring and Kimball, *J. Chem. Phys.*, 1, 239, 626 (1933); see also, Pauling, *ibid*, 1, 280 (1933).

simplify the derivation; these are particularly convenient for systems involving more than four electrons. The procedure that must be followed in the application of the rules is first to write down the bond arrangements corresponding to the bond eigenfunctions involved in the integral. For example, in the integral H_{AA} the two bond eigenfunctions are of the type A , and the bond systems are both $a-b$ $c-d$. A start is now made by assigning a spin of α arbitrarily to the a 's, then the spin of the b 's must be β , since combination of an α with a β is required for bond formation. Thus, giving a definite spin to the a 's fixes that of the b 's, but not that of any other electron; a and b are then said to form a *cycle*, which is designated by the symbol (a/b) . For later requirements, the numerator contains the orbital associated with spin α , and the denominator that associated with spin β . An arbitrary spin α is now assigned to c ; then d must have the spin β , so that (c/d) forms another cycle. The cycle system for the matrix component H_{AA} is thus $(a/b)(c/d)$. It may be remarked that this procedure is really a method for finding the number of antisymmetric eigenfunctions that the two bond functions have in common; since the spin in each cycle could have been chosen arbitrarily in two ways, the number is equal to 2^x , where x is the number of cycles. The matrix element involving the bond eigenfunctions is now found by means of the following general expression in which y is the number of bonds:

$$H_{LM} = \frac{2^x}{2^y} [Q + \frac{3}{2} \{ \sum J(\alpha/\beta) - \sum J(\alpha, \beta) \} - \frac{1}{2} \sum J_{ij}], \quad (24.28)$$

where

$\sum J(\alpha/\beta)$ = sum of single-exchange integrals between electrons in the same cycle with opposite spins

$\sum J(\alpha, \beta)$ = sum of single-exchange integrals between electrons in the same cycle with the same spin

$\sum J_{ij}$ = sum of all single-exchange integrals.

Equation (24.28) may now be applied to the evaluation of H_{AA} , in which the two cycles are (a/b) and (c/d) , with a and b , and also c and d , having opposite spins; since x is 2 and y is also 2, as there are two bonds, it is found that

$$\begin{aligned} H_{AA} &= \frac{2^2}{2^2} [Q + \frac{3}{2} \{ (ab) + (cd) - 0 \} \\ &\quad - \frac{1}{2} \{ (ab) + (cd) + (ac) + (bd) + (ad) + (bc) \}] \\ &= Q - \frac{1}{2} \{ (ac) + (bd) + (ad) + (bc) \} + (ab) + (cd), \end{aligned} \quad (24.29)$$

in exact agreement with equation (24.27). The same procedure gives for H_{BB} the result

$$H_{BB} = Q - \frac{1}{2} \{ (ab) + (cd) + (ad) + (bc) \} + (ac) + (bd). \quad (24.30)$$

For the determination of H_{AB} it must be remembered that the two bond systems A and B are different; if an arbitrary spin α is assigned to a , then b must have spin β in both systems, as shown below.



In this case there is now no complete cycle, for c must have spin β (to give the bond $a-c$ in B) and d must have spin α (to form the bond $b-d$); the complete spin assignment is thus



There is consequently one cycle only, represented by (ad/bc) , and application of equation (24.28) gives

$$\begin{aligned}
 H_{AB} &= \frac{2}{2^2} [Q + \frac{3}{2}\{(ab) + (ac) + (bd) + (cd) - (ad) - (bc)\} \\
 &\quad - \frac{1}{2}\{(ab) + (ac) + (bd) + (cd) + (ad) + (bc)\}] \\
 &= \frac{1}{2}\{Q + (ab) + (ac) + (bd) + (cd)\} - (ad) - (bc). \quad (24.31)
 \end{aligned}$$

There remains now, finally, the evaluation of the Δ 's, the matrix components of unity; these are given by expressions analogous to those for H_{AA} , H_{AB} and H_{BB} , such as equation (24.26), except that the operator is unity. In other words, the matrix components H_{II} , H_{III} , etc. are replaced by Δ_{II} , Δ_{III} , etc., defined by

$$\Delta_{II} = \int \psi_I \psi_I d\tau, \quad \Delta_{III} = \int \psi_I \psi_{III} d\tau, \text{ etc.}, \quad (24.32)$$

the antisymmetric eigenfunctions being real. If the approximation is made of taking the eigenfunctions, ψ_I , ψ_{II} , etc., to be normalized and mutually orthogonal, terms such as Δ_{II} , for the matrix component between identical eigenfunctions, are unity, while those, such as Δ_{III} , between different eigenfunctions, are zero. It follows, therefore, utilizing equation (24.26), that

$$\begin{aligned}
 \Delta_{AA} &= \frac{1}{4}(\Delta_{II} + \Delta_{III III} + \Delta_{IV IV} + \Delta_{V V}) \\
 &= \frac{1}{4}(1 + 1 + 1 + 1) = 1. \quad (24.33)
 \end{aligned}$$

It can be readily seen that, in general, the value of Δ_{ij} is equal to the coefficient of Q in the corresponding expression for H_{ij} ; hence, from equation (24.30), $\Delta_{BB} = 1$, and from (24.31) $\Delta_{AB} = \frac{1}{2}$.

24g. Evaluation of Energy.—The values for the various H 's and Δ 's may now be inserted into the secular equation (24.9), and the resulting quadratic

equation solved for E ; it is then found that

$$E = Q \pm \left[\frac{1}{2} \{ (ab) + (cd) - (ac) - (bd) \}^2 + \frac{1}{2} \{ (ac) + (bd) - (bc) - (ad) \}^2 + \frac{1}{2} \{ (bc) + (ad) - (ab) - (cd) \}^2 \right]^{1/2}. \quad (24.34)$$

Of the two solutions, represented by the plus and minus signs, the one with the plus sign represents the lowest energy value, since the coulombic and exchange integrals are negative,²⁷ and this should correspond, within the accuracy of the variation treatment, to the actual state of the four-electron system.

For certain purposes, it is convenient to replace the exchange (resonance) integrals (ab) and (cd) by α_1 and α_2 , (ac) and (bd) by β_1 and β_2 , and (bc) and (ad) by γ_1 and γ_2 ; respectively. The symbols α and β as used here have, of course, no connection with the spin eigenfunctions. Equation (24.34) then becomes

$$E = Q + \left[\frac{1}{2} \{ (\alpha_1 + \alpha_2) - (\beta_1 + \beta_2) \}^2 + \frac{1}{2} \{ (\beta_1 + \beta_2) - (\gamma_1 + \gamma_2) \}^2 + \frac{1}{2} \{ (\gamma_1 + \gamma_2) - (\alpha_1 + \alpha_2) \}^2 \right]^{1/2}, \quad (24.35)$$

and if α is written for $\alpha_1 + \alpha_2$, β for $\beta_1 + \beta_2$ and γ for $\gamma_1 + \gamma_2$, it is seen that

$$E = Q + \left[\frac{1}{2} \{ (\alpha - \beta)^2 + (\beta - \gamma)^2 + (\gamma - \alpha)^2 \} \right]^{1/2}. \quad (24.36)$$

The result obtained in this manner can be readily adapted to a system of three electrons, i.e., with three orbitals, such as a , b and c . The energy can be obtained from equation (24.34) by omitting all reference to d ; thus,

$$E = Q + \left[\frac{1}{2} \{ (ab) - (ac) \}^2 + \frac{1}{2} \{ (ac) - (bc) \}^2 + \frac{1}{2} \{ (bc) - (ab) \}^2 \right]^{1/2} \quad (24.37)$$

$$= Q + \left[\frac{1}{2} \{ (\alpha - \beta)^2 + (\beta - \gamma)^2 + (\gamma - \alpha)^2 \} \right]^{1/2}, \quad (24.38)$$

in which α , β and γ have been used for the exchange integrals (ab) , (ac) and (bc) , respectively. It will be observed that equations (24.36) and (24.38) are of exactly the same form.

For systems involving more than four electrons, the procedure adopted in calculating the energy, using antisymmetric electron eigenfunctions and bond eigenfunctions, is exactly similar to that described above. The same general rules are used to derive the canonical set of structures, the various eigenfunctions and the matrix components. The secular equation will, of course, be of the same order as the number of canonical structures. Some illustrations will be given in Section 26 in connection with the solution of the benzene and other problems. It may be remarked that if a system contains an odd number of electrons, it is treated as one with the next higher even number, and then the additional electron is assumed to be moved to infinity, so that all terms containing reference to it are ignored.

²⁷ This is because the corresponding forces are attractive at all reasonable internuclear distances (cf. Fig. 9).

24h. Determination of Resonance Energy.—The energy of the four-electron system as given by equation (24.36) takes into account the fact that there are two independent ways, represented by the structures A and B, of joining the electrons in pairs. In other words, it includes the contribution of the energy due to resonance among the two structures. The magnitude of this contribution can be estimated by calculating the energy for a single structure A or B, and comparing it with the value given by equation (24.36). For the structure A, for example, the energy E_A can be determined by [cf. equation (21.1)]

$$E_A = \frac{\int \psi_A H \psi_A d\tau}{\int \psi_A \psi_A d\tau} = \frac{H_{AA}}{\Delta_{AA}}. \quad (24.39)$$

Introducing the values of H_{AA} and Δ_{AA} given by equations (24.29) and (24.33), it follows that

$$\begin{aligned} E_A &= Q + (ab) + (cd) - \frac{1}{2}\{(ac) + (bd) + (ad) + (bc)\} \\ &= Q + \alpha_1 + \alpha_2 - \frac{1}{2}(\beta_1 + \beta_2 + \gamma_1 + \gamma_2) \\ &= Q + \alpha - \frac{1}{2}(\beta + \gamma). \end{aligned} \quad (24.40)$$

In exactly the same manner it can be shown that if the structure B had been the only one, the energy E_B would be given by

$$\begin{aligned} E_B &= Q + (ac) + (bd) - \frac{1}{2}\{(ab) + (cd) + (ad) + (bc)\} \\ &= Q + \beta - \frac{1}{2}(\alpha + \gamma). \end{aligned} \quad (24.41)$$

The resonance energy is equal to $E - E_A$, as given by equations (24.36) and (24.40) in the first case, and to $E - E_B$, given by equations (24.36) and (24.41) in the second case. Attention may be called to the fact that in equation (24.40), α , which is equal to $(ab) + (cd)$, represents the sum of the exchange integrals between bonded pairs of electrons, while $(\beta + \gamma)$, equal to $(ac) + (bd) + (ad) + (bc)$, is the sum of the exchange integrals between nonbonded pairs. The terms β and $(\alpha + \gamma)$ have, respectively, the same significance in equation (24.41). It follows, therefore, that when resonance among different structures is ignored or is absent, it is possible to write

$$E = Q + \sum_i J_{ii} - \frac{1}{2} \sum_{ij} J_{ij},$$

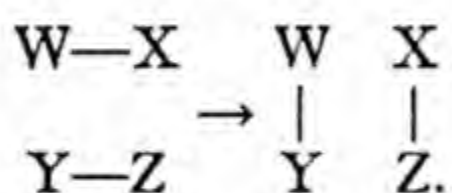
where J_{ii} and J_{ij} have the same significance as in the identical equation (19.10). The use of this expression to derive the energy of the water molecule in Section 22 is thus justified by the fact that there is only one reasonable way of coupling the electrons in the molecule of water, and consequently the question of resonance does not arise.

SYSTEMS OF SEVERAL ELECTRONS: APPLICATIONS

25. Activation Energy of Chemical Reaction.²⁸—An interesting application of the quantum mechanical treatment of systems involving several electrons is to the calculation of the energy of activation of a chemical reaction; this is the energy, in excess of the normal value, which must be acquired by reacting substances before they can undergo chemical change. Consider the reaction



in which the pairs of atoms W and X in WX, Y and Z in YZ, W and Y in WY, and X and Z in XZ are each joined by a two-electron bond. The reaction can, therefore, be regarded as a rearrangement of electron pairs, as may be seen by writing it in the form



The coupling of the electrons in the initial state is similar to the arrangement A on page 117, while in the final state it is similar to B. It must be remembered, however, that in the reactants the distances between W and Y, and X and Z, are large, while those between W and X, and Y and Z are small; in the products, the reverse will be the case. The problem is, therefore, to evaluate the energy of the four-electron system as the configuration changes from that represented by $WX + YZ$ to that implied by $WY + XZ$. From these changes information can be obtained concerning the activation energy of the reaction.

In principle, the method of solving this problem is to utilize equation (24.38), for the four-electron system, and to evaluate the coulombic and exchange integrals, using suitable eigenfunctions, for various internuclear distances. The situation is similar to that involved in the Heitler-London treatment of the hydrogen molecule (Section 15), except that it is now much more complicated. It is, in fact, so complex that a solution along these lines is almost out of the question, and an alternative, approximate, method has been proposed. Since it makes use of experimental data, in addition to the results of quantum mechanics, it is generally referred to as the *semi-empirical method* for calculating activation energies.

Suppose that in the four-electron system treated in Section 24, two of the electrons, e.g., c and d , were removed to an infinite distance from each other and from a and b . All terms involving c and d in equation (24.34) would then disappear, and the expression for the energy of the system would reduce to

$$E_{ab} = Q + (ab). \quad (25.1)$$

²⁸ Eyring and Polanyi, *Z. phys. Chem.*, B12, 279 (1931); Eyring, *J. Am. Chem. Soc.*, 53, 2537 (1931); for further details and applications, see Glasstone, Laidler and Eyring, "The Theory of Rate Processes."

The coulombic energy represents the interaction between the electrons a and b only, and this may be represented by the symbol A_1 ; similarly the exchange integral (ab) may be replaced by α_1 , so that

$$E_{ab} = A_1 + \alpha_1. \quad (25.2)$$

An analogous expression $E_{cd} = A_2 + \alpha_2$ can be obtained for the energy of the electrons c and d , with a and b at infinity, and similar equations can be derived for the other four possible ways of pairing the electrons, as shown in Fig. 18. The quantities A_1, A_2, B_1, B_2, C_1 and C_2 are the coulombic energies for the various electron pairs, and

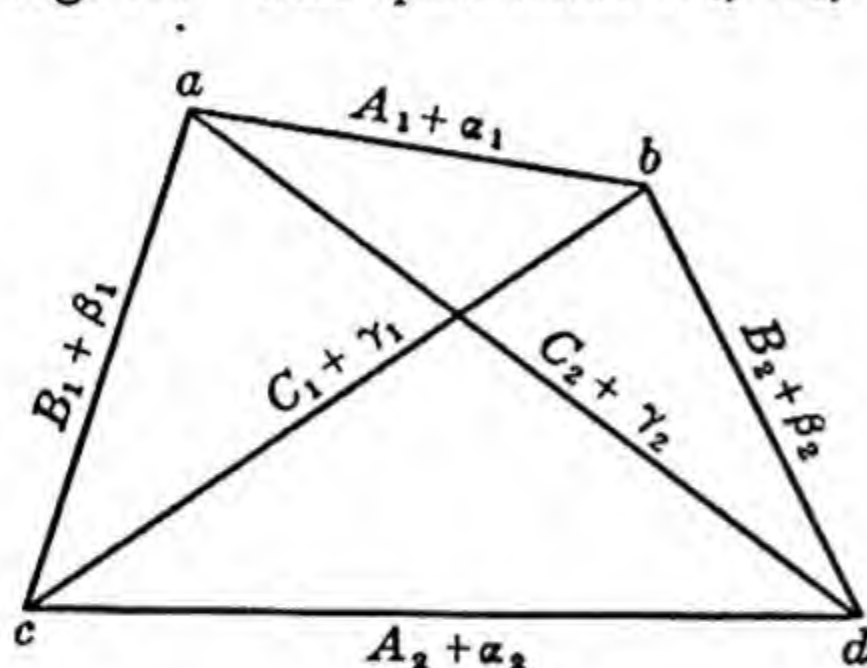


FIG. 18. Four electron problem

$\alpha_1, \alpha_2, \beta_1, \beta_2, \gamma_1$ and γ_2 , which have the same significance as in equation (24.35), are the corresponding exchange (resonance) energies. The coulombic (classical) energy is additive in character, and hence Q for the four-electron system, as it appears in equations (24.35) and (24.36), is equal to the sum of the six coulombic energies for the separate electrons pairs.

If the two electrons taking part in any pair, e.g., a and b , are both $1s$ electrons, it is evident that the equation (25.2) for the energy will be analogous to that which appears in the hydrogen molecule problem, equation (15.14). The approximation is made, therefore, of taking the ratio of the coulombic energy A_1 to the total energy $A_1 + \alpha_1$, as being equal to the same ratio in molecular hydrogen. According to the calculations of Sugiura, depicted graphically in Fig. 9, the coulombic energy is from 10 to 15 per cent of the binding energy of the hydrogen molecule, depending on the internuclear distance, provided the latter is not too small. It is supposed, therefore, as the basis of the semi-empirical calculation, that the coulombic energy is always a constant fraction, e.g., 15 per cent, of the total binding energy, irrespective of the internuclear distance and of the nature of the atoms concerned. The proportion of coulombic energy mentioned above is applicable, presumably, only if $1s$ electrons are involved; it appears from certain calculations that the proportion increases as the principal quantum number of the s electrons increases.

Now that a method is available of dividing the total energy into its constituent parts, the next problem is the determination of this energy for various internuclear distances. For this purpose use is made of spectroscopic data and the Morse equation (see Section 32b); this equation expresses the binding energy of a diatomic molecule as a function of the internuclear distance, and so it can be employed to calculate the separate coulombic and exchange energies. In the case of the reaction $WX + YZ = WY + XZ$, it would be necessary to have the Morse functions for six diatomic molecules,

viz., WX, YZ, WY, XZ, WZ and XY, and if these were available it would be possible to derive the separate quantities A_1, A_2, A_3, A_4, A_5 and A_6 , the sum of which is equal to Q , and $\alpha_1, \alpha_2, \alpha_3, \alpha_4, \alpha_5$ and α_6 , for any desired interatomic distances. With these data, the corresponding energies of the four-electron system could then be readily determined from equation (24.35). In this way, the nature of the energy path from the initial to the final state could be traced, and the energy of the intermediate or activated state could be determined.

Because of the large number of independent internuclear distances involved in the reaction between four atoms, the results are not easy to interpret, but the general nature of the procedure may be readily understood in the case of the reaction



involving three atoms, each supposed to possess a 1s electron available for bond formation. By means of three Morse equations, for the diatomic molecules XY, YZ and XZ, and the assumption made above concerning the proportion of coulombic energy, it is possible to derive all the information necessary for the evaluation of the energy of the three-electron system by means of equation (24.38). This energy is calculated as a function of the two internuclear distances Y—Z and X—Y; in the initial state Y—Z is small while X—Y is large, but in the final state the reverse is the case. The calculations are simplified by assuming a linear configuration of the atoms X, Y and Z, since it can be shown that this arrangement is the one requiring a minimum of energy. The results are then plotted in the form of a contour diagram, with the X—Y distances as abscissae and the Y—Z distances as ordinates, the various contour lines passing through points of equal energy. The *potential energy surface* obtained in this manner is found to consist of two valleys, each parallel to one of the axes, separated by a pass shaped somewhat like a saddle. It appears from the nature of this surface that as the atom X is brought up to the molecule YZ, by the most favorable reaction path, along the bottom of one of the valleys, the potential energy of the system increases at first slowly and then more rapidly until a maximum is reached at the top of the energy pass. The system can then continue down the bottom of the other valley, leading finally to the products XY and Z.

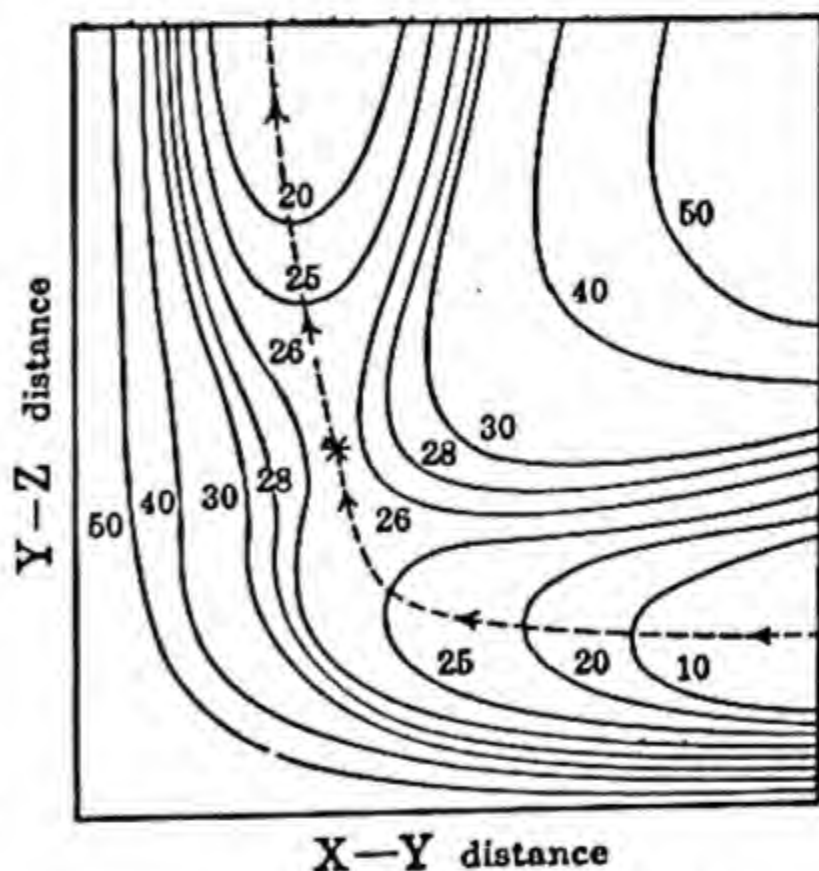


FIG. 19. Potential energy surface

(Fig. 19). The energy difference between the highest point of the path, i.e., the top of the pass, which gives the position of the activated state, and the level representing the reactants, is virtually equivalent to the energy of

activation of the reaction. Activation energies have been calculated in this manner for a number of reactions; on the whole the results are in fairly satisfactory agreement with experiment.

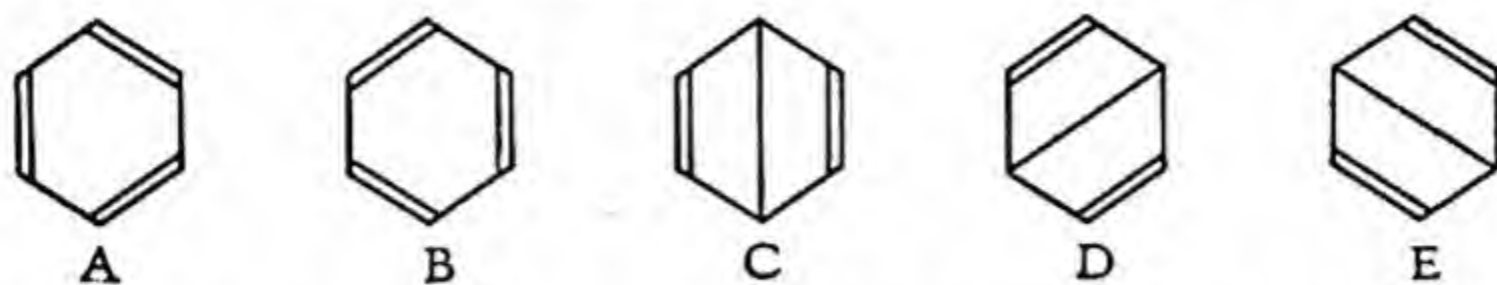
The question of activation energies may be considered in another, more approximate, manner. Taking the potential energy of an atom as zero, the energy of the reactant system $X + YZ$, with X at a large distance from YZ , is given by an equation similar to (25.1), i.e., $Q + \alpha$. As X is brought up nearer to YZ , the potential energy of the system increases, and when the activated state is reached the three atoms are close together. If the possibility of resonance is ignored, the energy would now be given by an expression identical with equation (24.40); since β and γ are negative, this energy is greater than that in the original state. The energy difference, equal to $\frac{1}{2}(\beta + \gamma)$, is approximately equivalent to the activation energy; β and γ are the resonance energies for XY and XZ , and the values depend on the distances between the nuclei in the activated state. The simple treatment outlined in this paragraph differs from the more detailed calculations described above, because the latter takes into account the resonance which occurs in the activated state when the three (or four) atoms are close together. The energy of activation is thus less than would have been the case had there been no resonance.

26a. The Benzene Problem.²⁹—It was seen in Section 20f that in benzene each carbon atom may be supposed to have three trigonal orbitals, lying in the plane of the benzene ring, while a fourth, pure $2p$, orbital projects at right angles to this plane. The energy of the electrons occupying the trigonal orbitals and their interaction with the electrons in the p -orbitals may be neglected. In any event, these quantities appear to the same extent in all the structures of the benzene molecule considered below, and their inclusion leads merely to a change in the arbitrary zero of energy. The purpose of the following calculations is primarily to calculate the resonance energy in benzene, and this involves a difference between two energy terms; the position of the arbitrary zero will thus not affect the results. It will be adequate, therefore, to consider only the different modes of interaction in pairs of the electrons forming the pure $2p$ orbitals, or, in other words, the different possible $\pi\pi$ bonds. Five independent interactions, or groups of $\pi\pi$ bonds, based on the concept of localized pairs, are possible and these represent the canonical set of structures, as shown below. (The configurations C, D and E, involving electronic interactions over unusually large distances, e.g., the



²⁹ Pauling and Wheland, *J. Chem. Phys.*, 1, 362 (1933); see also, Sherman, *ibid.*, 2, 488 (1934); Wheland, *ibid.*, 3, 230 (1935); Hückel, *Z. Physik*, 70, 204 (1931).

para-para bond, are sometimes referred to as *excited structures*.) All other interactions can be shown to be represented by a linear combination of the five canonical structures. If the single ($\sigma\sigma$) bonds between the carbon atoms are included, these five structures of benzene are as follows:



The first two of these are seen to be identical with the two Kekulé structures.

The eigenfunction for the six p electron system of benzene may be represented as a linear combination of the wave functions of the five canonical structures; thus,

$$\psi = a\psi_A + b\psi_B + c\psi_C + d\psi_D + e\psi_E \quad (26.1)$$

[see equation (17.7)]. It will be seen later that the coefficients a and b are equal, and so also are c , d and e ; this is to be expected, since the structures A and B are equivalent, on the one hand, and C, D and E are equivalent, on the other hand. In any event, taking the most general case as represented by equation (26.1), the variation theorem may be applied to evaluate the energy of the benzene system, which may be regarded as resonating among the five structures, and also to determine the coefficients a , b , c , d and e .

In setting up the secular equation for the benzene problem, the same essential approximations are made as in the treatment of the four-electron problem in Section 24. The antisymmetrical eigenfunctions are taken to be normalized and mutually orthogonal, and all exchange (resonance) integrals involving more than one interchange of a pair of electrons are set equal to zero. Further, the problem is greatly simplified, without causing serious error, by neglecting all exchange integrals other than those involving an interchange of electrons on *adjacent* atoms. The secular equation for the problem is

$$\begin{vmatrix} H_{AA} - \Delta_{AA}E & H_{AB} - \Delta_{AB}E & H_{AC} - \Delta_{AC}E & H_{AD} - \Delta_{AD}E & H_{AE} - \Delta_{AE}E \\ H_{BA} - \Delta_{BA}E & H_{BB} - \Delta_{BB}E & H_{BC} - \Delta_{BC}E & H_{BD} - \Delta_{BD}E & H_{BE} - \Delta_{BE}E \\ H_{CA} - \Delta_{CA}E & H_{CB} - \Delta_{CB}E & H_{CC} - \Delta_{CC}E & H_{CD} - \Delta_{CD}E & H_{CE} - \Delta_{CE}E \\ H_{DA} - \Delta_{DA}E & H_{DB} - \Delta_{DB}E & H_{DC} - \Delta_{DC}E & H_{DD} - \Delta_{DD}E & H_{DE} - \Delta_{DE}E \\ H_{EA} - \Delta_{EA}E & H_{EB} - \Delta_{EB}E & H_{EC} - \Delta_{EC}E & H_{ED} - \Delta_{ED}E & H_{EE} - \Delta_{EE}E \end{vmatrix} = 0, \quad (26.2)$$

and by utilizing the method of cycles described in Section 24f, it can be readily shown that this equation becomes

$$\begin{vmatrix} (Q-E) + \frac{3}{2}\alpha & \frac{1}{4}(Q-E) + \frac{3}{2}\alpha & \frac{1}{2}(Q-E) + \frac{3}{2}\alpha & \frac{1}{2}(Q-E) + \frac{3}{2}\alpha & \frac{1}{2}(Q-E) + \frac{3}{2}\alpha \\ \frac{1}{4}(Q-E) + \frac{3}{2}\alpha & (Q-E) + \frac{3}{2}\alpha & \frac{1}{2}(Q-E) + \frac{3}{2}\alpha & \frac{1}{2}(Q-E) + \frac{3}{2}\alpha & \frac{1}{2}(Q-E) + \frac{3}{2}\alpha \\ \frac{1}{2}(Q-E) + \frac{3}{2}\alpha & \frac{1}{2}(Q-E) + \frac{3}{2}\alpha & (Q-E) & \frac{1}{4}(Q-E) + \frac{3}{2}\alpha & \frac{1}{4}(Q-E) + \frac{3}{2}\alpha \\ \frac{1}{2}(Q-E) + \frac{3}{2}\alpha & \frac{1}{2}(Q-E) + \frac{3}{2}\alpha & \frac{1}{4}(Q-E) + \frac{3}{2}\alpha & (Q-E) & \frac{1}{4}(Q-E) + \frac{3}{2}\alpha \\ \frac{1}{2}(Q-E) + \frac{3}{2}\alpha & \frac{1}{2}(Q-E) + \frac{3}{2}\alpha & \frac{1}{4}(Q-E) + \frac{3}{2}\alpha & \frac{1}{4}(Q-E) + \frac{3}{2}\alpha & (Q-E) \end{vmatrix} = 0, \quad (26.3)$$

where Q is the coulombic energy, and α is used to represent the single exchange integrals between adjacent atoms, viz., (ab) , (bc) , (cd) , (de) and (ef) , which are all equal in magnitude. The determinant (26.3) can be reduced to three linear factors

$$\begin{aligned} (Q - E) - 2\alpha = 0, & \quad (Q - E) - 2\alpha = 0 \\ \text{and} \quad Q - E = 0, & \end{aligned} \quad (26.4)$$

and the quadratic factor

$$(Q - E)^2 - 2(Q - E)\alpha - 12\alpha^2 = 0, \quad (26.5)$$

for which the solutions for $Q - E$ are 2α , 2α , 0 , $(1 - \sqrt{13})\alpha$ and $(1 + \sqrt{13})\alpha$. Since the exchange integral α has a negative value (cf. Section 24g), the solution $(1 - \sqrt{13})\alpha$ represents the state with the lowest energy; thus

$$\begin{aligned} Q - E &= (1 - \sqrt{13})\alpha, \\ \therefore E &= Q + (\sqrt{13} - 1)\alpha \\ &= Q + 2.6055\alpha. \end{aligned} \quad (26.6)$$

If the possibility of resonance among the five structures had not been taken into consideration, and the benzene molecule had been regarded as consisting of a single Kekulé form only, the secular equation would then have had the simple form

$$H_{AA} - E' = 0, \quad (26.7)$$

where E' is the energy of the Kekulé structure. Introducing the value of H_{AA} , which is the same as in equation (26.3), it follows that

$$\begin{aligned} Q + \frac{3}{2}\alpha - E' &= 0, \\ E' &= Q + 1.5\alpha. \end{aligned} \quad (26.8)$$

The additional energy resulting from resonance between the five independent canonical structures is equal to $E - E'$, as given by equations (26.6) and (26.8), and this is equal to 1.1055α . It will be seen later that this amounts to about 36 kcal. per mole, and so resonance makes an important contribution to the stability of the benzene molecule.

It may be noted that the result given in equation (26.8) for a single Kekulé structure, without the effect of resonance, can also be obtained directly from equation (19.10), viz.,

$$E' = Q + \sum_i J_{ii} - \frac{1}{2} \sum_{ij} J_{ij} \quad (26.9)$$

Considering only the $\pi\pi$ bonds, and neglecting all exchange integrals involving nonadjacent atoms, it is evident that $\sum J_{ii}$ for bonded atoms is 3α , and $\sum J_{ij}$ for nonbonded atoms is also 3α ; hence,

$$E' = Q + 1.5\alpha,$$

as before.

It is of interest to calculate the value of the energy E'' of the benzene system if resonance occurred only between the two Kekulé structures A and B; the secular equation for this case is

$$\begin{vmatrix} (Q - E'') + \frac{3}{2}\alpha & \frac{1}{4}(Q - E'') + \frac{3}{2}\alpha \\ \frac{1}{4}(Q - E'') + \frac{3}{2}\alpha & (Q - E'') + \frac{3}{2}\alpha \end{vmatrix} = 0, \quad (26.10)$$

and hence the lowest energy is found to be given by

$$E'' = Q + 2.4\alpha. \quad (26.11)$$

The resonance energy for the two Kekulé structures is thus $E'' - E'$, i.e., 0.9α , compared with the total resonance energy of 1.055α . The two Kekulé forms A and B thus contribute about 85 per cent of the energy due to resonance, while 15 per cent is contributed by the three excited structures C, D and E.

Evaluation of the coefficients a , b , c , d and e in equation (26.1), by the usual variation method procedure described in Section 14c, shows that a and b are equal, and if these are taken as unity, the coefficients c , d and e are each 0.4341; so that

$$\psi = (\psi_A + \psi_B) + 0.4341(\psi_C + \psi_D + \psi_E). \quad (26.12)$$

The probability of any structure is proportional to the square of its coefficient in the complete eigenfunction ψ ; hence the total probability of the two Kekulé structures A and B is given by

$$\frac{2 \times 1^2}{(2 \times 1^2) + \{3 \times (0.4341)^2\}} = 0.78.$$

The probability of the electronic configuration of the benzene molecule being that of one or other of the two Kekulé structures is thus 0.78, compared with 0.22 for the three excited structures.

If it had been assumed originally that the coefficients a and b were the same, and that c , d and e were also equal, the fifth order determinant representing the secular equation (26.3), could have been reduced to one of the second order, viz.,

$$\begin{vmatrix} \frac{5}{2}(Q - E) + 6\alpha & 3(Q - E) + 9\alpha \\ 3(Q - E) + 9\alpha & \frac{5}{2}(Q - E) + 9\alpha \end{vmatrix} = 0. \quad (26.13)$$

The lowest of the two solutions is

$$E = Q + (\sqrt{13} - 1)\alpha,$$

in agreement with the result given by equation (26.6).

26b. Molecular Orbital Treatment of Benzene.³⁰—As in the localized pair method in the preceding section, the benzene problem considered by the method of molecular orbitals involves six $2p$ wave functions, one for each of the carbon atoms. Each electron is regarded as moving in the field produced by the nuclei and all the electrons other than itself. The eigenfunction (molecular orbital) for a *single electron* in the benzene system can then be represented by a linear combination of the wave functions $\psi_1, \psi_2, \psi_3, \psi_4, \psi_5$ and ψ_6 , of the six separated electrons. Assuming the latter orbitals to be normalized and orthogonal to each other, the secular equation for the system becomes

$$\begin{vmatrix} H_{11}-E & H_{12} & H_{13} & H_{14} & H_{15} & H_{16} \\ H_{21} & H_{22}-E & H_{23} & H_{24} & H_{25} & H_{26} \\ H_{31} & H_{32} & H_{33}-E & H_{34} & H_{35} & H_{36} \\ H_{41} & H_{42} & H_{43} & H_{44}-E & H_{45} & H_{46} \\ H_{51} & H_{52} & H_{53} & H_{54} & H_{55}-E & H_{56} \\ H_{61} & H_{62} & H_{63} & H_{64} & H_{65} & H_{66}-E \end{vmatrix} = 0, \quad (26.14)$$

where E is now the energy of a single electron in the potential field of the remainder of the molecule. Since the electrons are all equivalent, it is evident that the coulombic integrals $H_{11}, H_{22}, H_{33}, H_{44}, H_{55}$ and H_{66} will all be equal, and their value may be represented by q ; thus

$$H_{ii} = \int \psi_i \mathbf{H} \psi_i d\tau = q. \quad (26.15)$$

The suffix i refers to any one of the six electrons, and hence may have the value 1, 2, 3, 4, 5 or 6. The Hamiltonian operator \mathbf{H} is the one appropriate to the field in which each electron moves. The resonance integrals involving exchange of electrons between adjacent carbon atoms are $H_{12}, H_{23}, H_{34}, H_{45}, H_{56}$ and H_{61} , and the corresponding matrix components lying on the other side of the diagonal are $H_{21}, H_{32}, H_{43}, H_{54}, H_{65}$ and H_{16} . These are all equal and may be represented by β ; thus

$$H_{ij} = \int \psi_i \mathbf{H} \psi_j d\tau = \beta, \quad (26.16)$$

where j is equal to $i \pm 1$. All the other exchange integrals, involving the eigenfunctions of electrons on nonadjacent atoms, are assumed to be zero. The secular equation (26.14) thus reduces to

$$\begin{vmatrix} q-E & \beta & 0 & 0 & 0 & \beta \\ \beta & q-E & \beta & 0 & 0 & 0 \\ 0 & \beta & q-E & \beta & 0 & 0 \\ 0 & 0 & \beta & q-E & \beta & 0 \\ 0 & 0 & 0 & \beta & q-E & \beta \\ \beta & 0 & 0 & 0 & \beta & q-E \end{vmatrix} = 0. \quad (26.17)$$

³⁰ Wheland, *J. Chem. Phys.*, 2, 474 (1934); see also, Hückel, *Z. Physik*, 72, 310 (1931); 76, 628 (1932).

The general solution of an equation of this type, which will, incidentally, represent the secular equation for the molecular orbital treatment of any system involving more than two equivalent electrons, is given by

$$q - E = -2\beta \cos \frac{2\pi j}{n}, \quad (26.18)$$

where n is number of rows (or columns) in the determinant, i.e., the number of electrons in the system, and j will have a series of values $1, 2, 3, \dots, n$, for the n solutions. In the present case n is 6, and it can be readily shown, since the exchange integral β is negative, that the three lowest roots are

$$\begin{aligned} E &= q + 2\beta, \\ E &= q + \beta \end{aligned}$$

and

$$E = q + \beta. \quad (26.19)$$

The eigenfunctions corresponding to these three lowest eigenvalues can each have two electrons of opposite spin assigned to them; this is merely a consequence of the Pauli principle and does not mean to imply localized pairs. The total energy of the six $2p$ electrons in benzene is thus taken as twice the sum of the three lowest roots, that is, $6q + 8\beta$. If the benzene molecule had consisted of a single Kekulé structure, so that each $2p$ electron could be regarded as associated with only one adjacent $2p$ electron, the molecular orbital for a single electron would be a linear combination of two wave functions, e.g., ψ_1 and ψ_2 , ψ_3 and ψ_4 , or ψ_5 and ψ_6 . The energy of a single electron may then be obtained by the solution of any one of three secular equations of the type

$$\begin{vmatrix} q - E & \beta \\ \beta & q - E \end{vmatrix} = 0, \quad (26.20)$$

the lowest root of which gives

$$E = q + \beta. \quad (26.21)$$

The total energy of the system of six electrons would then be $6q + 6\beta$, and hence the resonance energy for the benzene molecule would be equal to 2β .

26c. Comparison of Localized Pair and Molecular Orbital Treatments.—It will be observed that according to the method of electron pairs the resonance energy of the benzene molecule is 1.106α , whereas the molecular orbital treatment gives 2β for the same quantity. Although both α and β have been referred to as "exchange" or "resonance" integrals, it is important to remember that they have quite different meanings. The integral α is the matrix component of the Hamiltonian operator between two antisymmetric (determinantal) eigenfunctions for the whole system, while in β the eigenfunctions are the atomic orbitals for single electrons. The integral α involves the exchange of two electrons between the orbitals on two atoms, and hence is similar to the resonance energy in the hydrogen molecule; β ,

on the other hand, is the integral for exchange of one electron between two orbitals, as in the hydrogen molecule-ion. The ratio of the bond energies in H_2^+ and H_2 is about 0.59, and since these energies are largely due to resonance, it is to be expected that the β/α will have about the same value. From the results obtained with benzene this ratio is seen to be $1.106/2$, i.e., 0.553.

A further comparison of the localized pair and molecular orbital methods may be made by calculating the resonance energies in terms of α and β , respectively, in other cases. As the number of $2p$ electrons in the molecule increases, the number of canonical structures increases rapidly. For example, with naphthalene there are 42 independent structures possible, representing different ways of pairing the ten $2p$ electrons. A complete solution of the problem by the method of localized valence bonds would thus require the solving of a secular equation of the 42nd order. Special methods have been devised, however, which simplify the calculations. In the molecular orbital treatment the naphthalene problem can be solved much more readily; the general equation (26.18) is employed, with n equal to 10, and the five lowest energy values are found.

The resonance energies derived by the two methods, in terms of the exchange integrals, α and β , are recorded in Table VI for a number of com-

TABLE VI. CALCULATED RESONANCE ENERGIES

Compound	Electron Pair Method	Molecular Orbital Method	$\frac{\beta}{\alpha}$
Cyclobutadiene	1.000α	0	∞
Benzene	1.106α	2.00β	0.553
Cyclooctatetrene	1.290α	1.66β	0.777
Biphenyl	2.37α	4.38β	0.541
Naphthalene	2.04α	3.68β	0.555
Styrene	1.31α	2.42β	0.541
Stilbene	2.59α	4.88β	0.531
Butadiene	0.232α	0.47β	0.494

pounds. The ratio of β/α in the last column is calculated on the assumption that the resonance energies obtained by the two methods are equal. It is apparent that, in general, the value of β/α is approximately constant; in fact, for all the stable molecules studied, with the exception of cyclobutadiene and cyclooctatetrene, β/α was found to lie between 0.477 and 0.555. The two methods of studying resonance, that is, by the localized pair and molecular orbital treatments, thus lead to approximately the same results in most instances. Where there is a difference, particularly in the case of cyclobutadiene, it is difficult to decide which treatment is the more reliable.

According to the electron pair method, the resonance energy in cyclobutadiene should be almost the same as in benzene; the two rings, C_4H_4 and C_6H_6 , would thus be expected to have somewhat similar stabilities. As is well known, however, the benzene ring is highly stable, whereas the C_4H_4 ring does not exist; this is in better agreement with the molecular orbital method which indicates that there is no resonance energy involved in cyclobutadiene. The experimental facts would imply that the molecular

orbital treatment was superior in this case. It has been pointed out, however, that the stability of ring compounds of the type $(CH)_n$ is not determined merely by interaction of the $2p$ electrons; an important factor is also the binding energy of the three other electrons of each carbon atom.³¹ By making the appropriate allowance for the latter, it is found that benzene should be the most stable ring structure of the type under consideration, with cyclooctatetrene as next. The instability of the cyclobutadiene ring is presumably due to the considerable strain involved in a structure with carbon bond angles of 90° . It is thus possible that in certain cases the molecular orbital method may give apparently better results than the localized electron-pair treatment because of the fortuitous cancellation of errors. However, it must be admitted that the former procedure is generally very much simpler and can be used when the latter method is too complicated to be carried through to a complete solution.

It must be borne in mind that some variation in the ratio β/α is not altogether unexpected. An examination of the significance of these integrals shows that there is no reason why α or β should be the same for different compounds. Variations in the correct eigenfunctions and in the energy operators will account for differences in the exchange integrals. This may possibly account for some, although not for all, of the observed discrepancies between the two methods of calculating resonance energies.

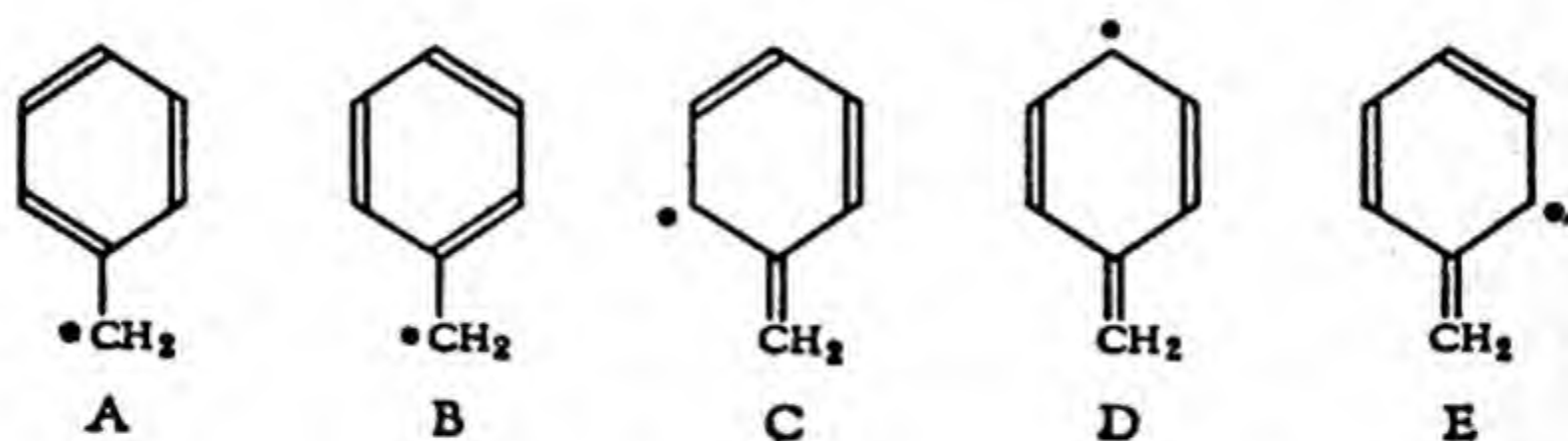
26d. Experimental Determination of Resonance Energies.³²—Since the direct evaluation of the integrals α and β presents great difficulties, empirical methods have been used to obtain some indication of their magnitudes. It has been found that when a molecule has a single valence-bond structure, that is to say, when there is no possibility of resonance between different electronic configurations, the heat of formation of the compound can be obtained with a fair degree of accuracy by summation of the known energies of the constituent bonds. On the other hand, in every case where there is reason for believing that resonance occurs, the experimental heat of formation of the molecule is greater than the value calculated from the bond energies. This additional energy whereby the molecule is stabilized is taken as equal to the resonance energy. Consider, for example, the molecule of benzene; the actual heat of formation from its constituent atoms is 1039 kcal. per mole, but the sum of the bond energies is only 1000 kcal. The resonance energy of the benzene molecule is thus about 39 kcal. per mole. This figure cannot be regarded as highly accurate because of the uncertainties in the bond energies, but a more reliable estimate can be made in another manner. The heat of hydrogenation of the one double bond in cyclohexene, in which molecule there is no resonance, is 28.59 kcal.; hence for three double bonds, as in benzene, the heat of hydrogenation to cyclohexane should be $3 \times 28.59 = 85.77$ kcal. The experimental value is 49.80 kcal., and hence the difference, equal to 35.97 kcal., is the additional energy possessed by a mole of benzene as a result of resonance.

³¹ Penney, *Proc. Roy. Soc., A*, 146, 223 (1934).

³² Pauling and Sherman, *J. Chem. Phys.*, 1, 679 (1933); Pauling, ref. 11.

According to the results obtained previously, the resonance energy in benzene should be 1.106α , and so the exchange integral α has a value in the region of 34 kcal. per mole. Almost identical results have been derived from data on the heats of formation of naphthalene, anthracene and phenanthrene. In an exactly similar manner, the resonance integral β is found to be equal to 20 kcal. per mole. It may be observed that the value of the exchange integrals in molecular hydrogen and in the hydrogen molecule-ion, which should be analogous to α and β , are about 85 kcal. and 60 kcal., respectively. These results serve to show that the values of α and β may well vary with the nature of the compounds. Their apparent constancy mentioned above probably arises from the fact that the results were obtained from compounds related to each other.

26e. Free Radicals.³³—A successful explanation of the stability of free radicals has been made on the basis of the postulate that the free valence resonates between several atoms in the radical. Consider the simple case of the phenylmethyl radical $C_6H_5CH_2\cdot$; five unexcited structures are possible, viz.,



the dot representing the position of the odd electron in each case. A number of excited structures can also exist, but as such structures generally make a small contribution to the resonance energy, they can be neglected in order to simplify solution of the problem. For the purpose of calculating the resonance energy the system may be treated as one involving the interaction of seven $2p$ electrons, one from each of the six carbon atoms in the ring, with the odd electron making the seventh. The fifth order secular equation can then be derived by the method of localized pairs using the procedure described in Section 24, with the modification necessary for an odd number of electrons. To simplify the solution of this equation, application is made of the fact that the structures A and B are equivalent, and so also are C and E; although D is different from C and E it may be assumed to be equivalent to them without serious error. The eigenfunction for the system then becomes

$$\psi = a(\psi_A + \psi_B) + c(\psi_C + \psi_D + \psi_E), \quad (26.22)$$

and the fifth order secular equation reduces to a quadratic, as in the analo-

³³ Pauling and Wheland, *J. Chem. Phys.*, 1, 362 (1934); 2, 482 (1935); Hückel, *Z. Physik*, 83, 632 (1933); *Trans. Faraday Soc.*, 30, 40 (1934).

gous case of the benzene molecule [equation (26.13)]. The equation is now

$$\begin{vmatrix} \frac{5}{2}(Q - E) + \frac{1}{2}\alpha & \frac{1}{2}(Q - E) + \frac{5}{2}\alpha \\ \frac{1}{2}(Q - E) + \frac{5}{2}\alpha & \frac{1}{2}(Q - E) + 10\alpha \end{vmatrix} = 0, \quad (26.23)$$

and the lowest solution is

$$E = Q + 2.409\alpha. \quad (26.24)$$

If resonance occurred between the two Kekulé structures A and B only, the secular equation would be

$$\begin{vmatrix} (Q - E') + \alpha & \frac{1}{2}(Q - E') + \frac{1}{2}\alpha \\ \frac{1}{2}(Q - E') + \frac{1}{2}\alpha & (Q - E') + \alpha \end{vmatrix} = 0 \quad (26.25)$$

and then

$$E' = Q + 1.9\alpha. \quad (26.26)$$

The resonance energy resulting from the three structures C, D and E, which are characteristic of the free radical, is thus $E - E'$ which is equal to 0.509α ; this has been called the *free radical resonance energy*.

Since the resonance integral α is about 34 kcal. in benzene derivatives, the stabilization energy of the phenylmethyl radical resulting from resonance between the three structures C, D and E is thus approximately 18 kcal. per mole. The energy required to break a C—C bond is normally about 70 kcal., and hence the heat of dissociation of sym.-diphenylethane is 70 kcal. minus the resonance energy of the two resulting free phenylmethyl radicals; the value of the dissociation energy should then be about 34 kcal. per mole. The tendency for diphenylethane to dissociate into two free radicals is thus not very great. On the other hand, calculations carried out in the manner described above show that the free radical resonance energy in triphenylmethyl is 1.108α , which is about 38 kcal. In this radical there are nine positions, three in each phenyl group, between which the odd electron can resonate; the stabilization energy is thus considerably greater than in the phenylmethyl radical. The resonance energy for two triphenylmethyl rad-

TABLE VII. STABILITIES AND RESONANCE ENERGIES IN FREE RADICALS

Free Radical	Resonance Energy
Phenylmethyl	0.509α
Biphenylmethyl	0.556α
β -Naphthylmethyl	0.631α
α -Naphthylmethyl	0.751α
Diphenylmethyl	0.841α
Triphenylmethyl	1.108α

icals is thus 76 kcal., which is of the order of magnitude of the energy of dissociation of a C—C bond. It follows, therefore, that hexaphenylethane should dissociate readily into free radicals, in agreement with experiment.

The magnitude of the resonance energy of a free radical may be taken as a measure of its stability; there should thus be a parallelism between these two properties. In Table VII are given the resonance energies of a number

of free radicals calculated by the electron pair method; the order is that of increasing stability, as derived from other sources. The resonance energy is seen to increase with increasing stability of the free radical.

It may be mentioned that calculations of the resonance energy of free radicals have also been made by the molecular orbital procedure in the manner already described. The agreement between the results obtained by the two methods is generally satisfactory, although the ratio β/α is found to vary from 0.587 to 0.927.

CHAPTER IV

MOLECULAR SPECTRA: DIATOMIC MOLECULES¹

BAND SPECTRA

27a. Types of Band Spectra.—The spectra of gaseous molecules appear as bands which are observed in three more or less distinct regions of the spectrum; these regions are (i) the ultra-violet or visible, (ii) the near (short wave length) infra-red, and (iii) the far (long wave length) infra-red. Although in many cases the bands have been resolved into a large number of closely spaced lines, and in other cases the resolution may be inferred, molecular spectra are still frequently referred to as *band spectra* to distinguish them from atomic spectra, i.e., line spectra. In order to account for the three types of band spectra and for their fine structure, it is postulated that the internal energy of a molecule, that is, energy other than translational, is essentially of three kinds, namely electronic, vibrational and rotational. Each of these forms of energy is quantized, so that certain eigenvalues only are possible; in other words, the molecules may be regarded as possessing certain discrete energy states. As a first approximation, the three forms of internal energy may be treated as independent, so that the states of any one form of energy do not depend on the values of the other energies. When a transition occurs from any energy state of a molecule to another state, as a result of the absorption or emission of energy, the spectrum of that molecule will exhibit a spectral line of frequency, in sec.^{-1} , equal to the energy change $E' - E''$ divided by the Planck constant h . It is the general practice in spectroscopic work to express frequencies (ν) in *wave numbers*, i.e., cm.^{-1} , so that

$$\nu = \frac{E' - E''}{hc} \text{ cm.}^{-1} \quad (27.1)$$

where c is the velocity of light.

27b. Electronic Spectra.—It is well known that the critical potential of an atom, that is the potential which must be applied to an electron in an atom to raise it from one principal quantum level to another, or to eject it completely, is generally in the region of 5 to 10 volts. It appears from various considerations, that a potential of the same order is required to change the energy level of an electron in a molecule; the energy difference between two electronic states of a molecule is thus about 5 to 10 electron volts (e.v.). Assuming, for purposes of calculation, an energy difference of 5 e.v., which is equivalent to about 8×10^{-12} erg per molecule, the frequency

¹ Herzberg, "Molecular Spectra and Molecular Structure: Diatomic Molecules"; Jevons, "Report on Band Spectra of Diatomic Molecules"; Sponer, "Molekülspektren"; Sutherland, "Infra-Red and Raman Spectra."

of the radiation accompanying the corresponding electronic transition is given by equation (27.1) as

$$\begin{aligned}\nu &= \frac{8 \times 10^{-12}}{6.6 \times 10^{-27} \times 3 \times 10^{10}} \\ &= 4 \times 10^4 \text{ cm.}^{-1}.\end{aligned}$$

A frequency of $4 \times 10^4 \text{ cm.}^{-1}$ is equivalent to a wave length of 2500 Å, and so the spectrum accompanying an electronic transition in a molecule, just as with an atom, should appear in the ultra-violet or short-wave visible portion of the spectrum. The molecular spectra observed in these regions are thus due to transitions from one electronic state to another, and are consequently referred to as *electronic spectra*. As will be seen shortly, the structure of the electronic bands is to be attributed to vibrational and rotational transitions accompanying the change in electronic energy.

In each electronic state there are a number of possible vibrational states corresponding to different values of the vibrational energy of the molecule. The energy difference between two successive vibrational levels of the same electronic state is of the order of 0.1 e.v. Further, the energy of rotation of the molecule about two (for a linear molecule) or three axes is quantized, and so it may be supposed that each vibrational level has a set of rotational sublevels. The energy difference between two adjacent rotational levels, in one and the same vibrational and electronic state, is in the vicinity of 0.005 e.v.

Suppose a normal molecule, in the ground state, receives sufficient energy to bring about a transition to a higher electronic (excited) state; if there were no changes in the vibrational and rotational energies accompanying this transition, the corresponding electronic spectrum would consist of a single line in the ultra-violet or short-wave visible region. In practice, however, each electronic change is accompanied by a vibrational energy change, the magnitude of which is determined by the vibrational levels in the initial (ground) and final (excited) electronic states. The vibrational energy quantum is generally about 0.1 e.v., as mentioned above, while the electronic change is about 5 e.v., and so it follows that the electronic spectrum of the molecule appearing in the region of 2500 Å, will consist of a number of lines with a spacing of approximately 50 Å. Simultaneously with the electronic and vibrational energy changes, there will be rotational transitions, and for a given electronic and vibrational change, every rotational transition will produce a line in the electronic spectrum. Since rotational quanta are of the order of 0.005 e.v., the spacing of these rotational lines will be about 2.5 Å. The set of rotational lines corresponding to a particular vibrational transition constitutes a *band*, and every different vibrational transition yields a band of this type. The whole system of vibrational bands for a particular electronic change is called a *band group* or *band system*. Each electronic transition that occurs under certain conditions of excitation will yield such a band system, and the series of systems or groups for the different possible electronic changes constitutes the band spectrum of the molecule.

It will be evident from the foregoing discussion that electronic spectra may be very complex, even if there is only one electronic transition. In general, a nonlinear molecule can have $3n - 6$ different modes of vibration (see Section 34a), where n is the number of atoms in the molecule, and each mode will produce a band group. In addition, for a nonlinear molecule, there will be rotations about three axes. It is evident, therefore, that in spite of certain restrictions, the so-called selection rules, the electronic spectrum of a polyatomic molecule will be very complex. It can be readily understood why little progress has yet been made in this field of spectroscopy. With diatomic molecules, however, the situation is greatly simplified, for two reasons; first, such molecules have but one vibrational mode, and, second, they have two identical moments of inertia at right angles, while the third is zero. Considerable progress has thus been made in the analysis of the electronic band spectra of diatomic substances, although relatively little work has been done hitherto on polyatomic molecules.

27c. Infra-Red Spectra.—Even when there is no change of electronic energy, there is the possibility of a transition from one vibrational energy level to another within the same electronic (ground) state of the molecule. As seen above, such a transition would be accompanied by an energy change of about 0.1 e.v., or 1.6×10^{-18} erg per molecule. The frequency of the radiation corresponding to such an energy change would be

$$\begin{aligned}\nu &= \frac{1.6 \times 10^{-18}}{6.6 \times 10^{-27} \times 3 \times 10^{10}} \\ &= 8 \times 10^2 \text{ cm.}^{-1},\end{aligned}$$

and this would represent a wave length of 125,000 Å or 12.5 μ , where the symbol μ represents 1 micron, i.e., 10^{-3} mm. The radiations accompanying vibrational changes within the electronic ground state should thus appear in the near infra-red portion of the spectrum. The spectral bands found in this region may, therefore, be attributed to vibrational transitions in the molecule.

As is the case with electronic changes, the transition from one vibrational state to another within a particular electronic state, e.g., the ground state, is associated with various possible rotational changes which lead to the presence of a number of closely spaced spectral lines. The near infra-red spectrum of a molecule thus appears, under low dispersion, as a continuous band, but with high resolving power the individual lines, due to the superposition of rotational energy changes on a particular vibrational transition, can often be distinguished. The *vibration-rotation bands* that result in this manner are generally observed in absorption; they are found in the wave length region of about 1 to 23 μ .

A diatomic molecule has only one mode of vibration, and so there is one vibration-rotation band for each vibrational transition; it will be seen later that the number of such transitions is not large, and so the near infra-red spectra are relatively simple. With increasing number of atoms in the

molecule the complexity increases, because of the large number of vibrational modes. In spite of the difficulties, considerable success has been achieved in the study of vibration-rotation spectra of polyatomic molecules; this subject will be treated more fully in the next chapter.

The theory developed here has so far provided an interpretation of two of the three types of molecular spectra mentioned earlier; there still remains the third type, observed in the far infra-red region. These bands, which occur at wave lengths of $200\ \mu$ or more, are due to transitions involving very small energy changes, namely about 0.005 e.v. It seems, therefore, that the far infra-red spectra must be attributed to transitions that are purely rotational in character, unaccompanied by changes in electronic or vibrational energy. The bands in the far infra-red are thus called *rotation spectra*. Each possible rotational energy change will produce a line in the rotation band, but the number of such lines is limited by the selection rules. The rotation spectra thus have the great advantage of simplicity of structure, but owing to the enormous experimental difficulties associated with spectroscopic studies in the far infra-red region, relatively little work has been done in this connection.

27d. Spectral Transition Probabilities.—Before proceeding to a more detailed discussion of the various types of spectra, it is important to consider under what conditions the production of such molecular spectra is possible. It can be shown by the methods of quantum mechanics that the probability of a transition between two energy states, indicated by the letters m and n , accompanied by the absorption or emission of (dipole) radiation, is determined by the matrix element P_{mn} ; this has components in the x , y and z directions, the one in the x direction being defined by

$$P_{mn(x)} = \int \psi_m^* (\sum_j e_j x_j) \psi_n d\tau, \quad (27.2)$$

where ψ_m and ψ_n are the eigenfunctions of the two states (the asterisk, as before, representing the complex conjugate); e_j is the electric charge and x_j the x coordinate of the j th atom in the molecule. The summation of $e_j x_j$ over all the atoms in the molecule gives the component of the electric dipole moment in the direction of the x axis, i.e., μ_x , so that

$$P_{mn(x)} = \int \psi_m^* \mu_x \psi_n d\tau. \quad (27.3)$$

If the probability of a particular transition is not to be zero, then at least one of the three components of P_{mn} must differ from zero; if all three vanish, the given transition cannot occur, and there will consequently be no corresponding line in the spectrum.

Apart from any other considerations, there is one particular condition under which the integral giving the component of the matrix element vanishes; this arises when the component μ_x of the dipole moment is zero in

the equilibrium state of the molecule and remains so throughout the various movements of electrons and nuclei. In other words, if a molecule is symmetrical in its ground state, so that it possesses no resultant dipole moment, it will not interact with radiation, and hence it will not yield a spectrum, unless the symmetry of the electrons or of the nuclei can be disturbed in such a manner as to produce an electric moment.

Consider, for example, a symmetrical diatomic molecule, such as H_2 or O_2 ; such a molecule has a resultant dipole moment of zero, and this value is not changed in the course of vibration or rotation of the molecule. The movement of the electrons is so rapid compared with that of the nuclei that when a molecule vibrates or rotates the electrical center of each atom remains unaffected. The dipole moment is therefore changed only if the symmetry of the molecule is altered, and this cannot occur with a diatomic molecule. It follows, therefore, that a symmetrical diatomic molecule cannot undergo transitions that lead to changes in vibrational and rotational energies only. The molecule is incapable of interacting with radiation of the frequencies corresponding to energy changes of this type. This means that a homopolar diatomic molecule will yield no vibration-rotation or pure rotation spectrum. No infra-red spectra have, in fact, been observed for molecules of the type under consideration.

Although these substances do not exhibit vibration-rotation and pure rotation spectra, they do possess electronic spectra. The reason for this occurrence is that the acquisition of electronic energy is accompanied by a change in the configuration of the electrons which leads to a resultant dipole moment. Since the molecule is now no longer electrically symmetrical, it can also interact with the radiation in such a way as to bring about vibrational and rotational transitions. It can thus be understood why symmetrical diatomic molecules produce electronic spectra, complete with vibrational bands and rotational lines, in spite of the fact that the infra-red spectra of such molecules are inactive. Nuclear symmetry, however, as distinct from the lack of electronic symmetry, results in certain rotational levels being absent. Diatomic molecules possessing a resultant electrical dipole moment in their ground states, e.g., NO , HCl , OH , CN , etc., exhibit all three types of molecular spectra.

A symmetrical polyatomic molecule, such as CH_4 (tetrahedral), BCl_3 (planar) or CO_2 (linear) remains nonpolar in the course of rotational motion; molecules of this type will thus not exhibit pure rotation spectra. However, certain of the vibrations of symmetrical polyatomic molecules are active in the near infra-red, so that vibration-rotation bands are observed. Some of the vibrational modes, even of molecules that are symmetrical in their equilibrium states, are accompanied by nuclear displacements that destroy the symmetry and produce resultant dipole moments. Not all the modes of vibration will be active, but even for such a symmetrical molecule as methane, some of the vibrations are able to interact with infra-red radiation. If the polyatomic molecule possesses a resultant dipole moment in its ground state it will, of course, exhibit pure rotation as well as vibration-rotation

spectra. All polyatomic molecules, like diatomic molecules, exhibit electronic band spectra, irrespective of whether they are polar or nonpolar in their normal states.

ROTATION SPECTRA

28a. Rigid Rotator.—As already indicated, because of the small number of vibrational and rotational degrees of freedom, the spectra of diatomic molecules are relatively simple. For this reason, it is convenient in the discussion of molecular spectra to consider diatomic and polyatomic molecules separately. The knowledge gained from the study of diatomic molecules, which will be undertaken first, will be found of value in the interpretation of the complex spectra of molecules containing more than two atoms (Chapter V).

As a first approximation, a rotating diatomic molecule, whose nuclei are considered as being separated by a definite mean distance, may be treated as a rigid rotator with free axis. As shown in Section 9f, the permitted values for the energy of such a rotator can be stated in the form of the equation

$$E_r = \frac{h^2}{8\pi^2 I} J(J+1), \quad (28.1)$$

where J , called the *rotational quantum number*, is zero or integral, and I is the moment of inertia of the molecule about the axis of rotation. If a rotational transition occurs from an upper level, with quantum number J' , to a lower level, of quantum number J'' , the energy emitted is given by

$$E'_r - E''_r = \frac{h^2}{8\pi^2 I} \{J'(J'+1) - J''(J''+1)\}. \quad (28.2)$$

The frequency of the corresponding spectral line, expressed in wave numbers, is then given by equation (27.1) as

$$\nu_r = \frac{h}{8\pi^2 I c} \{J'(J'+1) - J''(J''+1)\} \quad (28.3)$$

$$= B \{J'(J'+1) - J''(J''+1)\}, \quad (28.4)$$

where the constant B , called the *rotational constant*, is defined by

$$B = \frac{h}{8\pi^2 I c} \text{ cm.}^{-1}. \quad (28.5)$$

The actual value of the frequency ν_r depends on B , which is a characteristic property of the molecule, since it involves the moment of inertia, and also on the two quantum numbers J' and J'' . It is in the latter connection that consideration of the transition probabilities, by means of wave mechanics, leads to a simple but important result. Insertion of the appropriate eigenfunctions for a rigid rotator, derived in Section 11, for the upper and

lower states in equation (27.3), and assuming, of course, that μ_z is not zero, it is found that $P_{mn(x)}$ will be zero unless $J' - J'' = \pm 1$. In other words, the only rotational transitions that are permitted, are those involving an increase or decrease of unity in the rotational quantum number. The *selection rule* for rotational transitions may thus be stated as

$$\Delta J = \pm 1, \quad (28.6)$$

where ΔJ is equal to $J' - J''$.

If in a rotational transition the quantum number in the initial state is J , and that in the final state is $J - 1$, in accordance with the selection rule, then substitution in equation (28.4) gives the result

$$\nu_r = 2BJ, \quad \text{where} \quad J = 1, 2, 3, \dots, \text{etc.} \quad (28.7)$$

The lowest value of J must be unity for two reasons; in the first place, if J were zero, $J - 1$ would be negative, and, in the second place, when J is zero the corresponding frequency given by equation (28.7) would be zero. Since J can be 1, 2, 3, etc., it follows that the frequencies of consecutive lines in the pure rotation spectrum of a diatomic molecule are $2B, 4B, 6B$, etc. On the frequency (wave number) scale, therefore, the lines are equally spaced, the constant frequency separation between successive lines being equal to $2B$, i.e., to $h/4\pi^2 Ic \text{ cm.}^{-1}$.

28b. Nonrigid Rotator.—Experimental investigation has shown that the successive lines in the far infra-red spectrum are not evenly spaced, but that the frequency separation decreases slightly with increasing J values. The actual frequencies can be expressed with a fair degree of accuracy by means of the equation

$$\nu_r = bJ - dJ^3, \quad (28.8)$$

where b and d are constants, d being much less than b . For example, the lines in the pure rotation spectrum of hydrogen chloride are represented by

$$\nu_r = 20.79 J - 0.0016 J^3.$$

It is apparent that the discrepancy between experiment and theory is to be ascribed to the assumption that the molecule behaves as a rigid rotator. As the nuclei can vibrate with respect to one another, the diatomic molecule cannot be rigid, and hence equation (28.1) for the rotational energy is inadequate. By allowing for the fact that increasing the rotational energy increases the moment of inertia of the molecule because of the centrifugal force, it is possible to derive the equation

$$E_r = BJ(J + 1)hc - DJ^2(J + 1)^2hc \quad (28.9)$$

for the eigenvalues of the rotational energy, where B has the same significance as before, equation (28.5), and D is a constant approximately represented by

$$D = \frac{4B^3}{\omega^3}$$

in which ω is the vibration frequency of the molecule in its normal state (cf. Section 29a). Since B is generally about 10 cm.^{-1} , whereas ω is of the order of 1000 cm.^{-1} , it is evident that D will be small, namely 10^{-3} cm.^{-1} or so. Introducing the selection rule, $\Delta J = \pm 1$, and assuming the transition $J \rightarrow J - 1$, it is readily shown from equation (28.9) that the frequencies of the rotational lines for a nonrigid diatomic molecule will be given by

$$\nu_r = 2BJ - 4DJ^3, \quad (28.10)$$

which is of the same form as the empirical equation (28.8).

28c. Internuclear Distances.—From the point of view of the chemist the particular interest of rotational spectra lies in the fact that they may be used to calculate the moment of inertia, and hence the internuclear distance of the diatomic molecule. From the frequency separations of the rotational lines it is possible to evaluate B , and hence the moment of inertia I may be derived from the definition, equation (28.5). As seen in Section 9b, the moment of inertia of a diatomic molecule is related to the reduced mass μ by the equation

$$I = \mu r^2, \quad (28.11)$$

where r^2 is here the mean square distance between the centers of gravity of the nuclei. The reduced mass μ may be derived from the masses of the atoms constituting the molecule [equation (9.17)], and so the internuclear distance r may be calculated from spectroscopic data. Some of the results obtained in this manner are recorded in Table VIII.

TABLE VIII. INTERNUCLEAR DISTANCES FROM ROTATION SPECTRA

Substance	$B \text{ cm.}^{-1}$	$I \text{ g. cm.}^2$	$r \text{ cm.}$
Hydrogen fluoride	20.57	1.34×10^{-40}	0.92×10^{-8}
Hydrogen chloride	10.40	2.66	1.28
Hydrogen bromide	8.35	3.31	1.42
Hydrogen iodide	6.42	4.31	1.62

28d. Isotope Effect in Rotational Spectra.—An isotopic exchange does not affect the internuclear distance in a diatomic molecule, but the change in mass results in an alteration of the moment of inertia. The rotational energy values, and the frequency separation of successive lines in the rotational spectrum, are consequently different for different isotopic forms of the same molecule. Neglecting the effect of centrifugal force, the frequencies of rotational lines are expressed by equation (28.7), and if the value of B , equation (28.5), is inserted, it follows that

$$1\nu_r = \frac{h}{4\pi^2 I_{1c}} J \quad (28.12)$$

and

$$2\nu_r = \frac{h}{4\pi^2 I_{2c}} J, \quad (28.13)$$

where the subscripts 1 and 2 refer to two isotopic forms of the same molecule. It follows, therefore, that the *isotopic shift*, that is, the frequency shift $\Delta\nu_i$ resulting from the isotopic change, is given by

$$\Delta\nu_i = \frac{h}{4\pi^2c} J \left(\frac{1}{I_1} - \frac{1}{I_2} \right).$$

Dividing through by equation (28.12), and abbreviating ${}_{1\nu_r}$ to ν_r , it is seen that

$$\frac{\Delta\nu_i}{\nu_r} = 1 - \frac{I_1}{I_2}. \quad (28.14)$$

The ratio of the moments of inertia, which is equal to the ratio of the reduced masses, since the internuclear distances are constant, is represented by the symbol ρ^2 , thus

$$\frac{I_1}{I_2} = \frac{\mu_1}{\mu_2} = \rho^2, \quad (28.15)$$

and so equation (28.14) becomes

$$\Delta\nu_i = \nu_r(1 - \rho^2). \quad (28.16)$$

Since ν_r may be replaced, without serious error, by $2BJ$, [equation (28.7)], it follows that

$$\Delta\nu_i = 2BJ(1 - \rho^2). \quad (28.17)$$

For most diatomic molecules which exhibit pure rotation spectra, the isotopic masses are such that ρ^2 differs only slightly from unity; hence the isotopic shift is small. It may be noted, however, that according to equation (28.17) the isotopic shift becomes greater as the rotational quantum number J increases. Because of the experimental difficulties the displacement of the lines in the rotational spectrum accompanying an isotopic change has not been observed, but it will be seen shortly that evidence for the isotopic effect in rotation has been obtained from electronic and vibration-rotation bands.

VIBRATION-ROTATION SPECTRA

29a. Linear Harmonic Oscillator.—The eigenvalues for the energy of a linear harmonic oscillator, to which a vibrating diatomic molecule may be supposed to approximate, can be represented by an equation of the type of (8.43); this may be written as

$$E_v = (v + \frac{1}{2})h\omega, \quad (29.1)$$

where v is the vibrational quantum number, equal to zero or an integer, and ω is the vibration frequency of the oscillator expressed in wave numbers. If the vibrational and rotational energies do not interact, so that they may be

regarded as additive, the total vibrational and rotational energy is

$$E_{vr} = (v + \frac{1}{2})hc\omega + \frac{h^2}{8\pi^2I} J(J + 1). \quad (29.2)$$

Assuming for the present that in a transition from an upper vibrational level, in which the quantum number is v' , to a lower state, with quantum number v'' , there is no change in the rotational energy, then the vibrational energy change is given by

$$E'_v - E''_v = (v' - v'')hc\omega. \quad (29.3)$$

The frequency ν_v of the radiation, in wave numbers, accompanying the vibrational transition, would then be obtained by dividing the energy change by hc , so that

$$\nu_v = (v' - v'')\omega. \quad (29.4)$$

Assuming the diatomic molecule to have a permanent dipole moment, for otherwise it would possess no vibration-rotation spectrum, the probability of a given transition can be found, as before, by inserting the appropriate eigenfunction for a linear harmonic oscillator, equation (8.44), into equation (27.3). It is found in this manner that the result differs from zero only if the change in the vibrational quantum number in the two states taking part in the transition is equal to unity. It follows, therefore, that for a harmonic oscillator, the selection rule is

$$\Delta v = \pm 1. \quad (29.5)$$

Utilization of this result in connection with equation (29.4) gives

$$\nu_v = \omega, \quad (29.6)$$

so that for a harmonic oscillator the frequency ν_v of the radiation emitted or absorbed should be equal to the mechanical frequency ω of vibration of the system, in agreement with the requirements of classical electrodynamics. According to equation (29.6) the vibration spectrum should consist of a single line, provided there are no accompanying rotational energy changes; as will be seen shortly, the rotational transitions result in the formation of a series of lines in the vicinity of the fundamental frequency given by equation (29.6). For reasons to be explained later, the line for which ν_v is equal to ω is generally missing in the vibration-rotation spectra of diatomic molecules. The corresponding frequency is, however, referred to as the *origin* or *center* of the band.

29b. Anharmonic Vibrations.—If the change in the vibrational quantum number were restricted to unity, as would be the case for a strictly harmonic oscillator, each mode of vibration in the molecule would yield one band only. The vibration-rotation spectrum of a molecule would thus consist of a single *fundamental band*, with $v' - v''$ equal to unity. Actually, investigation shows, that there is one strong band, but there are always one or two others,

called *overtones* or *harmonics*, with approximate frequencies to be expected if the change in the vibrational quantum number is 2, 3, etc. The interpretation of these facts is that the oscillations of the molecule are not truly harmonic, a conclusion in general agreement with other observations.

The vibrational potential energy V of a molecule may be expanded in the form of a Taylor series, thus

$$V = V_0 + \sum_i \left(\frac{\partial V}{\partial q_i} \right)_0 q_i + \frac{1}{2} \sum_{ij} \left(\frac{\partial^2 V}{\partial q_i \partial q_j} \right)_0 q_i q_j + \frac{1}{6} \sum_{ijk} \left(\frac{\partial^3 V}{\partial q_i \partial q_j \partial q_k} \right)_0 q_i q_j q_k + \cdots, \quad (29.7)$$

where q_i, q_j, q_k , etc., are the coordinates of the nuclei, i, j, k , etc.; the zero subscripts are used to indicate that V_0 and the various derivatives refer to the equilibrium state of the molecule. The potential energy V_0 is the value when all the nuclei are in their equilibrium positions, and if this is chosen as the arbitrary zero of energy, the first term in equation (29.7) may be eliminated. Further, in the equilibrium position, that is, at the minimum of the potential energy curve (see Section 32a),

$$\left(\frac{\partial V}{\partial q_i} \right)_0 = 0, \quad \text{where} \quad i = 1, 2, 3, \cdots, \quad (29.8)$$

and hence equation (29.7) may be written in the form

$$V = \frac{1}{2} \sum_{ij} b_{ij} q_i q_j + \frac{1}{6} \sum_{ijk} b_{ijk} q_i q_j q_k + \frac{1}{24} \sum_{ijkl} b_{ijkl} q_i q_j q_k q_l + \cdots, \quad (29.9)$$

where the constants b_{ij}, b_{ijk} , etc., are used for the second, third, etc., derivatives of V in equation (29.7). For a diatomic linear oscillator, equation (29.9) becomes simply

$$V = \frac{1}{2} k_1 q^2 + \frac{1}{6} k_2 q^3 + \frac{1}{24} k_3 q^4 + \cdots, \quad (29.10)$$

where q is the displacement from the equilibrium position during the oscillation. If Hooke's law is obeyed, so that the vibrations are truly harmonic in character, or, in general, if the vibrations are very small, equation (29.10) reduces to the familiar form, viz., $V = \frac{1}{2} k q^2$, used in the derivation of equation (29.1) (cf. Section 8). However, if the vibrations are not harmonic, it is necessary to go beyond the quadratic term in equation (29.10) in the expression employed for the potential energy when solving the wave equation for the linear oscillator. The derivation of the eigenvalues for the energy is now, naturally, more difficult, but the result obtained may be arranged so as to take the convenient form

$$E_v = (v + \frac{1}{2}) h c \omega_e - (v + \frac{1}{2})^2 h c x \omega_e + (v + \frac{1}{2})^3 h c y \omega_e + \cdots, \quad (29.11)$$

where x, y , etc., are the *anharmonicity constants*; the frequency ω_e is called

the *equilibrium frequency* of the molecule, which is the value for small displacements.

Besides modifying the expression for the energy of the oscillator, the use of equation (29.11) alters the corresponding eigenfunctions with the result that the matrix component, which determines the transition probability, is no longer zero for all transitions other than those for which the change in the vibration quantum number is unity. It has been shown that inclusion of the cubic term in equation (29.10) gives the selection rule $\Delta v = \pm 2$ and ± 4 , while the quartic term gives $\Delta v = \pm 3$ and ± 5 for permitted transitions. It follows, therefore, that in addition to the change of unity in the vibrational quantum number, leading to the formation of the fundamental band in the near infra-red spectrum, other transitions in which v changes by 2, 3, 4, etc., are possible for an anharmonic oscillator. The fundamental band is the one for which the transition is $v = 1$ to $v = 0$; for the transition $v = 2$ to $v = 0$, and $v = 3$ to $v = 0$, etc., which are now permitted, the corresponding bands are called the first overtone (second harmonic), second overtone (third harmonic), etc. The intensity of the band falls off with increasing value of Δv ; hence, the fundamental band is relatively strong, but the harmonics become increasingly feeble, so that it is rarely possible to detect overtone bands beyond the third.

As an approximation, the third term and those beyond it in equation (29.11) may be neglected so that the expression for the vibrational energy is

$$E_v = (v + \frac{1}{2})hc\omega_e - (v + \frac{1}{2})^2hc x \omega_e. \quad (29.12)$$

The energy change in a transition from the state v' to the state v'' is then

$$E'_v - E''_v = (v' - v'')hc\omega_e - \{v'(v' + 1) - v''(v'' + 1)\}hc x \omega_e,$$

so that the corresponding frequency is

$$\nu_v = (v' - v'')\omega_e - \{v'(v' + 1) - v''(v'' + 1)\}x\omega_e. \quad (29.13)$$

If the vibrational quantum number in the final state is always zero, the general equation for the fundamental and overtone bands is

$$\begin{aligned} \nu_{v \rightarrow 0} &= v\omega_e - \{v(v + 1)\}x\omega_e \\ &= \{1 - (v + 1)x\}v\omega_e, \end{aligned} \quad (29.14)$$

where v is the quantum number in the initial state. Setting v equal to 1, 2, 3, etc., there are obtained the following equations for the frequencies of the origins (or centers) of the fundamental (ν_1) and the first (ν_2) and second (ν_3) overtone bands:

$$\nu_1 = (1 - 2x)\omega_e \quad (29.15)$$

$$\nu_2 = (1 - 3x)2\omega_e \quad (29.16)$$

$$\nu_3 = (1 - 4x)3\omega_e. \quad (29.17)$$

It is seen that the frequencies of the origins of the fundamental, and first and second overtone vibration-rotation bands are approximately in the ratio of 1 to 2 to 3, since x is relatively small; the wave lengths are thus roughly in the proportion of 1 to $\frac{1}{2}$ to $\frac{1}{3}$. This fact is important, as the overtone bands appear in regions of shorter wave lengths than do the fundamental, and so they are more easily studied experimentally, in spite of their lower intensity.

If the positions of the origins of the various bands are determined spectroscopically, it is possible to evaluate both the equilibrium vibration frequency ω_e and the anharmonicity correction $x\omega_e$, for the diatomic molecule. The frequencies ν_1 , ν_2 , ν_3 and ν_4 for hydrogen chloride are 2885.9, 5668.0, 8347.0 and 10,922.7 cm^{-1} , respectively; from these the mean values of 2988.9 cm^{-1} for ω_e and 51.65 cm^{-1} for $x\omega_e$ have been calculated.

In the foregoing treatment the usual convention has been adopted of calculating the frequencies of *emission* bands, since ν' has been taken as being always greater than ν'' . Actually, however, vibration bands are almost invariably observed in *absorption*. The frequencies of such bands are given by exactly the same equations as for the emission spectra, the only difference being that the vibrational quantum numbers in initial and final states are reversed. The equations (29.15), (29.16) and (29.17) thus give the frequencies of the origins of the fundamental and overtone bands in absorption, the transitions being from $v = 0$ to $v = 1$, from $v = 0$ to $v = 2$, from $v = 0$ to $v = 3$, respectively. That the lower level of a vibrational absorption band is nearly always, if not always, zero, at least at ordinary temperatures, is due to the fact that under these conditions most of the molecules in a gas are in their lowest ($v = 0$) vibrational state. The absorption of radiation must, therefore, result in the transitions starting from $v = 0$, as observed. Theoretically, transitions such as $v = 1$ to $v = 2$, $v = 2$ to $v = 3$, and others, are permitted, but the proportion of molecules having vibrational quantum numbers greater than zero, at ordinary temperatures, is so small that the bands involving such molecules would be extremely faint. There is a possibility that bands of this kind might exist at higher temperatures, but the frequency of the $v = 1$ to $v = 2$ band would be so close to that of the $v = 0$ to $v = 1$ band that it is doubtful if the former (weaker) band could be detected. It may be remarked that electronic energy changes are often accompanied by transitions between levels with high v values; the energies concerned in these changes are, of course, very large in comparison with vibrational energy quanta.

29c. Fine Structure of Vibration-Rotation Bands.—In order to understand the rotational fine structure of the vibration bands, it will be convenient to consider, in the first place, the simple case in which the vibrational and rotational energies do not interact. If the oscillations are simple harmonic in character, and the molecule may be treated as a rigid rotator, the total vibrational and rotational energy will be given by equation (29.2). If there is a simultaneous transition from the vibrational level v' to the level v'' , and from the rotational level J' to the level J'' , the energy change

would be

$$E'_{vr} - E''_{vr} = (v' - v'')h\omega + \frac{h^2}{8\pi^2 I} \{J'(J' + 1) - J''(J'' + 1)\}, \quad (29.18)$$

and the corresponding spectral frequency would be

$$\nu = (v' - v'')\omega + B\{J'(J' + 1) - J''(J'' + 1)\}, \quad (29.19)$$

where B has the same significance as before, viz., $h/8\pi^2 Ic$. For the fundamental band, $v' - v''$ is unity, and the first term on the right-hand side, giving the origin of the band, would be $\omega \text{ cm.}^{-1}$, as required by equation (29.6). If the oscillations had been assumed to be anharmonic, and the appropriate expression for the energy had been employed, the first term in equation (29.19) would still give the origin of the band. In general, therefore, for the fundamental as well as for the overtone bands, it is possible to replace this term by ν_0 , representing the frequency of the origin (or center) of the band, as given by equation (29.14); hence equation (29.19) may be written as

$$\nu = \nu_0 + B\{J'(J' + 1) - J''(J'' + 1)\}. \quad (29.20)$$

According to the selection rule for rotational changes, ΔJ can be $+1$ or -1 , and the results obtainable from these two alternatives may be considered. If, in the first case, ΔJ is $+1$, then the rotational quantum number in the initial state (J') may be taken as $J - 1$, and in the final state (J'') as J ; in these circumstances, equation (29.20) gives

$$J - 1 \rightarrow J: \quad \nu(P) = \nu_0 - 2BJ, \quad \text{where} \quad J = 1, 2, 3, \dots \quad (29.21)$$

In the second case, when ΔJ is -1 , the initial state (J') may be represented by J and the final state (J'') by $J - 1$; the frequencies of the corresponding lines are then given by

$$J \rightarrow J - 1: \quad \nu(R) = \nu_0 + 2BJ, \quad \text{where} \quad J = 1, 2, 3, \dots \quad (29.22)$$

The results of equations (29.21) and (29.22) may be combined in the form

$$\nu = \nu_0 + 2Bm, \quad (29.23)$$

with

$$m = \pm 1, \pm 2, \pm 3, \dots$$

When m has the negative values, equation (29.23) reduces to the form of (29.21), which represents a series of lines, with a constant frequency separation of $2B \text{ cm.}^{-1}$, lying on the lower frequency (longer wave length) side of the center of the band whose frequency is $\nu_0 \text{ cm.}^{-1}$. These lines constitute the fine structure of what is known as the *P branch* of the vibration-rotation band. If m has the positive values in equation (29.23) the result is identical with (29.22); this gives a series of lines, called the *R branch*, with the same constant frequency separation of $2B \text{ cm.}^{-1}$ on the higher frequency (shorter

wave length) side of the center of the band. The complete vibration-rotation band should thus appear as a series of lines, equally spaced on the frequency scale, to the right and left of the center. It will be noted that the value of J in equation (29.23) cannot be zero, so that the line of frequency corresponding to the center of the band should be absent. These expectations are in agreement with experiment; the rotation-vibration bands of hydrogen chloride, for example, consist of a number of lines with an approximately constant frequency separation of $2B \text{ cm.}^{-1}$. At the center of the band, however, there is a gap, as expected, and the spacing between the lines lying immediately on each side of the center is thus $4B \text{ cm.}^{-1}$.

29d. The Q Branch.—If the reason for the absence of a line at the origin of the vibration-rotation bands of a diatomic molecule is sought, it will be found to lie in the fact that ΔJ can be only $+1$ or -1 . It would be necessary for ΔJ to be zero if the vibration-rotation spectrum were to have a line of frequency ν_0 . For all diatomic molecules, with the exception of nitric oxide (see below), the vibrational transition with $\Delta J = 0$ is forbidden; that is to say, for diatomic molecules a vibrational energy change must be accompanied by a rotational transition. It is of interest, therefore, to consider at this point the conditions under which a purely vibrational transition, that is, one with $\Delta J = 0$, is possible. If a molecule possesses a resultant orbital angular momentum Λ (see Section 2a), its figure axis will undergo a rotatory motion, similar to the astronomical phenomenon known as *nutation* (Fig. 20). Most diatomic molecules have Σ ground states, and so Λ is zero, and there is no rotation of the figure axis. For many polyatomic molecules, however, and for one diatomic molecule, viz., nitric oxide, Λ differs from zero; in these cases nutation occurs, and as a result the rotational energy is affected. For a diatomic molecule, a small constant term would be added to the value for the rigid rotator; hence the expressions for the frequencies of rotational lines would be unaffected, since these involve a difference between two energy values.



FIG. 20. Nutation of figure axis of molecule

For present purposes the important point to note is that if Λ is not zero, and the value does not alter in the transition under consideration, i.e., there is no electronic change, then the selection rule for changes in the rotational quantum number becomes

$$\Delta J = 0, \pm 1. \quad (29.24)$$

It is seen, therefore, that if a molecule possesses a resultant angular momentum, i.e., Λ is not zero, then a vibrational transition is possible without an accompanying change in the rotational quantum number. In this case, the line in the center of the vibration band, having the frequency given by

$$J \rightarrow J: \quad \nu(Q) = \nu_0, \quad (29.25)$$

appears in the spectrum, and is referred to as a *Q branch*. It might seem, as first sight, that the *Q branch* should consist of a single line in the center

of the band; however, this is not so, for it has been often observed to exhibit a definite fine structure. The explanation for the occurrence of this group of lines in the Q branch lies in the fact that the moment of inertia of the molecule differs in the two vibrational states taking part in the transition producing the band. This matter will be considered more fully in the next section, dealing with the interaction of vibrational and rotational motions.

29e. Interaction of Vibrational and Rotational Energies.—In the treatment so far, the possibility of interaction between vibrational and rotational energies has been ignored; however, such interaction is inevitable, for the mean distance of separation of the nuclei, and consequently the moment of inertia, will vary with the value of the vibrational energy, that is, with the vibrational quantum number. Taking into consideration, further, that a diatomic molecule behaves as a nonrigid rotator, equation (28.9) for the rotational energy may be modified so as to take the general form

$$E_r = B_v J(J+1)hc - D_v J^2(J+1)^2 hc, \quad (29.26)$$

where the values of B_v and D_v refer to the particular vibrational level indicated by the quantum number v . In the lowest level ($v = 0$), these become B_0 and D_0 ; they are then identical with the quantities B and D , respectively, in equation (28.9) for the rotational energy in the ground state.

The constant B_v may be defined in the usual manner by

$$B_v = \frac{h}{8\pi^2 I_v c}, \quad (29.27)$$

with I_v , the moment of inertia of the molecule in its v th vibrational level, given by

$$I_v = \mu r_v^2, \quad (29.28)$$

where r_v^2 is the mean square of the internuclear distance in that level. For the equilibrium state, when the amplitude of vibration is small, it is possible to define a quantity B_e ; thus

$$B_e = \frac{h}{8\pi^2 I_e c}, \quad (29.29)$$

where

$$I_e = \mu r_e^2, \quad (29.30)$$

and r_e refers to the internuclear distance in the equilibrium state of the molecule. It has been shown, by means of quantum mechanics, that B_v is related to the equilibrium value by the expression

$$B_v = B_e - \alpha_e(v + \frac{1}{2}) + \dots, \quad (29.31)$$

where α_e is a constant of the order of $0.02B_e$ to $0.05B_e$. It is apparent, therefore, that B_v will decrease with increasing vibrational quantum number, although the effect is generally negligible when v is small. In the same way, the constant D_v , which allows for the nonrigidity of the molecule, is related

to the equilibrium value D_e by

$$D_v = D_e + \beta_e(v + \frac{1}{2}) + \dots \quad (29)$$

Since β_e is small in comparison with D_e , which is itself small, the correction term may be ignored except in work of the highest precision.

The equation for the rotational energy may consequently be written

$$E_r = B_v J(J+1)hc - D_e J^2(J+1)^2 hc + \dots, \quad (29)$$

where D_e is regarded as constant for all vibrational levels. The total vibrational and rotational energy, allowing for interaction, is thus

$$E_{vr} = (v + \frac{1}{2})hc\omega_e - (v + \frac{1}{2})^2 hc x \omega_e + \dots + B_v J(J+1)hc - D_e J^2(J+1)^2 hc + \dots \quad (29)$$

From this equation the expressions for the frequencies of the lines constituting the P and R branches of a vibrational band are readily determined as follows:

$$J-1 \rightarrow J: \quad \nu(P) = \nu_0 - (B' + B'')J + (B' - B'')J^2 + 4D_e J^3 + \dots \quad (29)$$

$$J \rightarrow J-1: \quad \nu(R) = \nu_0 + (B' + B'')J + (B' - B'')J^2 - 4D_e J^3 + \dots, \quad (29)$$

where

$$J = 1, 2, 3, \dots$$

The constants B' and B'' are the values of B_v in the initial and final states involved in the vibrational transition. The frequency ν_0 is, as before, that of the center (origin) of the band.

If the molecule possesses a resultant angular momentum, so that a transition for which ΔJ is zero is possible, then the expression for the frequency of the Q branch is

$$J \rightarrow J: \quad \nu(Q) = \nu_0 + (B' - B'')J + (B' - B'')J^2, \quad (29)$$

where

$$J = 0, 1, 2, 3, \dots$$

This result accounts for the fact that the Q branch is observed to consist of a number of very closely spaced lines. If B' were equal to B'' , there would be only one line, but since these quantities are slightly different, in the different vibrational levels, a series of lines, each corresponding to a different value of J , will result. The difference $B' - B''$ must be small, particularly for the vibrational quantum numbers v' and v'' do not differ by more than 4 at most, and so the lines will be closely spaced. Attention should be called to the fact that in deriving equation (29.37) the influence of the nuclear spin on the rotational energy has been assumed to be the same in the initial and final vibrational levels; this is not strictly true, for the effect depends on the moment of inertia which is not constant. However, the error is small and is of no consequence in the present discussion.

of the band; however, this is not so, for it has been often observed to exhibit a definite fine structure. The explanation for the occurrence of this group of lines in the Q branch lies in the fact that the moment of inertia of the molecule differs in the two vibrational states taking part in the transition producing the band. This matter will be considered more fully in the next section, dealing with the interaction of vibrational and rotational motions.

29e. Interaction of Vibrational and Rotational Energies.—In the treatment so far, the possibility of interaction between vibrational and rotational energies has been ignored; however, such interaction is inevitable, for the mean distance of separation of the nuclei, and consequently the moment of inertia, will vary with the value of the vibrational energy, that is, with the vibrational quantum number. Taking into consideration, further, that a diatomic molecule behaves as a nonrigid rotator, equation (28.9) for the rotational energy may be modified so as to take the general form

$$E_r = B_v J(J+1)hc - D_v J^2(J+1)^2 hc, \quad (29.26)$$

where the values of B_v and D_v refer to the particular vibrational level indicated by the quantum number v . In the lowest level ($v = 0$), these become B_0 and D_0 ; they are then identical with the quantities B and D , respectively, in equation (28.9) for the rotational energy in the ground state.

The constant B_v may be defined in the usual manner by

$$B_v = \frac{h}{8\pi^2 I_v c}, \quad (29.27)$$

with I_v , the moment of inertia of the molecule in its v th vibrational level, given by

$$I_v = \mu r_v^2, \quad (29.28)$$

where r_v^2 is the mean square of the internuclear distance in that level. For the equilibrium state, when the amplitude of vibration is small, it is possible to define a quantity B_e ; thus

$$B_e = \frac{h}{8\pi^2 I_e c}, \quad (29.29)$$

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and r_e refers to the internuclear distance in the equilibrium state of the molecule. It has been shown, by means of quantum mechanics, that B_v is related to the equilibrium value by the expression

$$B_v = B_e - \alpha_e(v + \frac{1}{2}) + \dots, \quad (29.31)$$

where α_e is a constant of the order of $0.02B_e$ to $0.05B_e$. It is apparent, therefore, that B_v will decrease with increasing vibrational quantum number, although the effect is generally negligible when v is small. In the same way, the constant D_v , which allows for the nonrigidity of the molecule, is related

to the equilibrium value D_e by

$$D_v = D_e + \beta_e(v + \frac{1}{2}) + \dots \quad (29.32)$$

Since β_e is small in comparison with D_e , which is itself small, the correction term may be ignored except in work of the highest precision.

The equation for the rotational energy may consequently be written

$$E_r = B_v J(J+1)hc - D_e J^2(J+1)^2 hc + \dots, \quad (29.33)$$

where D_e is regarded as constant for all vibrational levels. The total vibrational and rotational energy, allowing for interaction, is thus

$$E_{vr} = (v + \frac{1}{2})hc\omega_e - (v + \frac{1}{2})^2 hc x \omega_e + \dots \\ + B_v J(J+1)hc - D_e J^2(J+1)^2 hc + \dots \quad (29.34)$$

From this equation the expressions for the frequencies of the lines constituting the P and R branches of a vibrational band are readily determined as follows:

$$J-1 \rightarrow J: \quad \nu(P) = \nu_0 - (B' + B'')J + (B' - B'')J^2 + 4D_e J^3 + \dots \quad (29.35)$$

$$J \rightarrow J-1: \quad \nu(R) = \nu_0 + (B' + B'')J + (B' - B'')J^2 - 4D_e J^3 + \dots, \quad (29.36)$$

where

$$J = 1, 2, 3, \dots$$

The constants B' and B'' are the values of B_v in the initial and final states involved in the vibrational transition. The frequency ν_0 is, as before, that of the center (origin) of the band.

If the molecule possesses a resultant angular momentum, so that the transition for which ΔJ is zero is possible, then the expression for the frequency of the Q branch is

$$J \rightarrow J: \quad \nu(Q) = \nu_0 + (B' - B'')J + (B' - B'')J^2, \quad (29.37)$$

where

$$J = 0, 1, 2, 3, \dots$$

This result accounts for the fact that the Q branch is observed to consist of a number of very closely spaced lines. If B' were equal to B'' , there would be only one line, but since these quantities are slightly different, in the two vibrational levels, a series of lines, each corresponding to a different value of J , will result. The difference $B' - B''$ must be small, particularly since the vibrational quantum numbers v' and v'' do not differ by more than 3 or 4 at most, and so the lines will be closely spaced. Attention should be drawn to the fact that in deriving equation (29.37) the influence of the nutation on the rotational energy has been assumed to be the same in the initial and final vibrational levels; this is not strictly true, for the effect depends on the moment of inertia which is not constant. However, the error is small and is of no consequence in the present discussion.

29f. Frequency Separation of Rotational Lines.—According to the simple treatment of Section 29c, in which the diatomic molecule is considered as a rigid rotator with independent rotational and vibrational energies, the frequency separation $\Delta\nu$ of successive lines in both P and R branches should be equal to $2B$ cm.⁻¹, i.e.,

$$\Delta\nu = 2B = \frac{h}{4\pi^2 I_c} \text{ cm.}^{-1}. \quad (29.38)$$

This result is identical with that for the frequency separation of the lines in the pure rotation spectrum (Section 28a). Hence the results obtained from the vibration-rotation spectrum may be utilized to evaluate the moment of inertia, and thus the internuclear distance, of the diatomic molecule.

In actual practice, because of the nonrigid nature of the rotating molecule and the interaction of vibrational and rotational energies, the frequency separations in the P and R branches are not constant. It can be readily shown from equation (29.35) that the frequency separation $\Delta\nu(P)$ of successive lines in the P branch of a vibration-rotation spectrum can be represented by

$$\Delta\nu(P) = 2B' - (B' - B'')2J + \dots, \quad (29.39)$$

the terms involving D being neglected because they are small. Similarly, from equation (29.36), the separation of the lines in the R branch is given by

$$\Delta\nu(R) = 2B' + (B' - B'')2J + \dots. \quad (29.40)$$

It follows, therefore, that the frequency separation of successive lines in the vibration band will not be constant in either branch. If $B' - B''$ is positive, the value of $\Delta\nu$ in the P branch should decrease with increasing J , that is, as the lines are further from the center of the band. On the other hand, in the R branch the separation should increase as J increases. If $B' - B''$ is negative, the reverse will, of course, be expected. The experimental facts are in agreement with these theoretical deductions.

The equations just derived for the frequency separations of the lines in the P and R branches of a vibration-rotation band are applicable for all types of bands, fundamental and overtones. For the fundamental band, v' is unity and v'' is zero; for the first overtone v' is 2 with v'' equal to zero, and so on. It is seen, therefore, that although the frequency separations of the rotational lines are approximately the same in different bands, they will not be exactly the same because of the difference in the B_v values.

From an analysis of the frequencies of the lines in the P and R branches of the various vibration-rotation bands of a given diatomic molecule, it is possible to determine the B_v values for two or three vibrational levels. From these, the rotation constant B_e , for the equilibrium state of the molecule, can be calculated from equation (29.31). As in the case of the pure rotation spectrum, the results may be used to evaluate the equilibrium moments of inertia and the corresponding nuclear separations. The data for the most

abundant isotopic form of each of the hydrogen halides are given in Table IX; these may be compared with the corresponding results quoted in Table VIII derived from pure rotation spectra.

TABLE IX. INTERNUCLEAR DISTANCES FROM VIBRATION-ROTATION SPECTRA

Substance	B_e cm. ⁻¹	I_e g. cm. ²	r_e cm.
Hydrogen fluoride	20.967	1.335×10^{-40}	0.9166×10^{-8}
Hydrogen chloride	10.591	2.644	1.2747
Hydrogen bromide	8.471	3.304	1.414
Hydrogen iodide	6.551	4.272	1.604

29g. Restoring Force in Diatomic Molecules.—If one of the two nuclei constituting a diatomic molecule is displaced, from its hypothetical rest position, along the line of the nuclei, the attractive force between them will cause the nuclei to oscillate with respect to each other. For small vibrations, at least, the restoring force exerted by one nucleus on the other will be proportional to their relative displacement; the nuclei will thus execute simple harmonic oscillations along the line joining them. Assuming the nuclei to act as point masses, situated at their centers of gravity, the vibrations of the diatomic molecule may be studied further by means of Fig. 21, in which x_1 and x_2 represent the displacements from their respective positions of rest of the nuclei of masses m_1 and m_2 , respectively. The relative displacement of the nucleus of mass m_1 with respect to the other is then $x_1 - x_2$, while that of the nucleus of mass m_2 is $x_2 - x_1$. If the oscillations are simple harmonic in character, as they probably will be for small vibrations (cf. Section 29b), the restoring forces will be $-k(x_1 - x_2)$ and $-k(x_2 - x_1)$, respectively, where k is the *force constant* of the system. Since the restoring force is also equal to the product of the mass and the acceleration, that is, to $m(d^2x/dt^2)$, it follows that



FIG. 21. Vibrating diatomic molecule

$$m_1 \frac{d^2x_1}{dt^2} = -k(x_1 - x_2) \quad (29.41)$$

and

$$m_2 \frac{d^2x_2}{dt^2} = -k(x_2 - x_1). \quad (29.42)$$

Writing x for $x_1 - x_2$, it follows that

$$\frac{d^2x}{dt^2} = \frac{d^2x_1}{dt^2} - \frac{d^2x_2}{dt^2}, \quad (29.43)$$

and introducing the results of equations (29.41) and (29.42), it is seen that

$$\frac{d^2x}{dt^2} = -kx \left(\frac{1}{m_1} + \frac{1}{m_2} \right). \quad (29.44)$$

Utilizing the definition of the reduced mass, equation (9.17), this becomes

$$\mu \frac{d^2x}{dt^2} = -kx. \quad (29.45)$$

If this is compared with equation (8.1), which holds for a single particle, it is readily found that the equation corresponding to (8.6) is now

$$k = 4\pi^2\nu^2\mu \quad (29.46)$$

where ν is the mechanical frequency of vibration of the harmonic oscillator.

As seen in Sections 29a and 29c, the frequency ν_0 of the center of the fundamental vibration band in the infra-red spectrum is equal to ω , the mechanical vibration frequency of the harmonic oscillator. It is thus possible to replace ν in equation (29.46) by the spectral frequency ν_0 . In general, however, the equilibrium frequency ω_e , which is determined from the spectrum, as already explained, may be used in place of ν_0 , since the former refers to the condition when the vibrations are small; hence, equation (29.46) becomes

$$k = 4\pi^2\omega_e^2\mu. \quad (29.47)$$

The importance of this expression lies in the fact that it may be employed to calculate the force constant, i.e., the restoring force per cm., for a diatomic molecule. This is a measure of the attractive force between the atoms, and hence is of interest to the chemist. The values of the force constants for the hydrogen halides, calculated from the equilibrium vibration frequencies ω_e obtained from their near infra-red spectra, are recorded in Table X. It

TABLE X. FORCE CONSTANTS IN HYDROGEN HALIDES

Substance	ω_e , cm. ⁻¹	k dynes per cm.	kr_e^2
Hydrogen fluoride	4141.3	9.59×10^6	8.13×10^{-11}
Hydrogen chloride	2988.9	5.16	8.05
Hydrogen bromide	2649.7	4.11	8.22
Hydrogen iodide	2309.5	3.14	8.14

is of interest to note that the values of the restoring forces for these substances are roughly inversely proportional to the square of the equilibrium internuclear distances, as shown by the approximate constancy of the quantity kr_e^2 in the last column of the table.

29h. Isotope Effect in Vibrational Bands.—It is probable that two isotopic forms of the same molecule have the same force constants; as they have different reduced masses, however, it is apparent from equation (29.47) that their equilibrium vibration frequencies will differ. If ω_1 and ω_2 represent the values of ω_e for the two isotopic forms, and μ_1 and μ_2 are their respective reduced masses, it follows from equation (29.47), that

$$\frac{\omega_2}{\omega_1} = \left(\frac{\mu_1}{\mu_2} \right)^{1/2} = \rho, \quad (29.48)$$

where ρ is defined as $(\mu_1/\mu_2)^{1/2}$, as in Section 28d. It follows, therefore, that

$$\omega_2 = \rho\omega_1. \quad (29.49)$$

Theoretical considerations show that the anharmonicity constant x is proportional to the equilibrium frequency [see equation (32.10)], so that it is possible to write

$$x_2 = \rho x_1, \quad (29.50)$$

analogous with equation (29.49). Utilizing equation (29.14), which is the general expression for the frequency of the center of any band involving the lower vibrational level of $v = 0$, it is seen, with the aid of equations (29.49) and (29.50), that

$${}_1\nu_{v \rightarrow 0} = v\omega_1 - \{v(v+1)\}x_1\omega_1 \quad (29.51)$$

and

$${}_2\nu_{v \rightarrow 0} = v\rho\omega_1 - \{v(v+1)\}\rho^2x_1\omega_1, \quad (29.52)$$

where the subscripts 1 and 2 refer to the two isotopic molecules. The isotopic shift $\Delta\nu_i$, which is the frequency difference of the centers of the two isotopic bands, is then given by the difference of the two frequencies in equations (29.51) and (29.52); thus,

$$\Delta\nu_i = (1 - \rho)\{1 - (v+1)\rho x_1\}v\omega_1. \quad (29.53)$$

For the fundamental band, v is 1 and this expression becomes

$$\Delta\nu_i(1) = (1 - \rho)(1 - 2\rho x_1)\omega_1,$$

whereas for the harmonics,

$$\Delta\nu_i(2) = (1 - \rho)(1 - 3\rho x_1)2\omega_1$$

and

$$\Delta\nu_i(3) = (1 - \rho)(1 - 4\rho x_1)3\omega_1.$$

It is evident, therefore, that if x and ω_e , that is, x_1 and ω_1 , are known for one isotopic molecule, it is possible to calculate the frequency shift for another isotopic form of the same diatomic molecule. It will be observed that the larger the value of $1 - \rho$, that is the more the ratio of the reduced masses differs from unity, the greater will be the isotopic shift.

The foregoing calculations give the alteration in the frequency of the origin of a vibrational band as the result of an isotopic change. However, since the expressions for the frequencies of the rotational lines in the band all involve the frequency of the origin as a constant term, it is apparent that all the lines will be shifted by the same amount as the origin. In other words, the effect of an isotopic exchange is to move the whole band bodily by an amount given by the equations derived above. If ρ is greater than unity, the isotopic shift $\Delta\nu_i$ is in the direction of lower frequency, whereas if it is less than unity the shift is in the opposite direction.

If a mixture of two isotopic molecules is studied, e.g., H^{35}Cl and H^{37}Cl , it is evident that the rotational lines for both forms will be present in the vibration bands. Every line should thus appear as a doublet, the frequency separation of which, to a first approximation, has the constant value $\Delta\nu_r$. Ordinary hydrogen chloride consists of a mixture of about three parts of H^{35}Cl to one part of H^{37}Cl , and in all the near infra-red bands of this gas that have been studied the rotational lines appear as doublets, one being appreciably stronger than the other. The observed isotopic frequency shifts have been found to be in good agreement with those calculated. It should be realized that the frequency separations of the doublets will not be exactly constant in any given band, because of the rotational isotopic effect mentioned in Section 28d. Strictly speaking, the total isotopic shift is the sum of the shifts given by equations (28.17) and (29.53). Since the former increases with the value of the rotational quantum number J , the separation of the rotational isotopic doublets in any band increases as the lines are further from the origin of the band.

The isotope of hydrogen chloride involving heavy hydrogen, i.e., DCl , presents a case of special interest. Because the atomic weight of deuterium is approximately twice that of the lighter isotope, the ratio of the reduced masses of the two forms of hydrogen chloride is about two; the isotopic shift is consequently exceptionally large. Thus a comparison of H^{35}Cl and D^{35}Cl shows that the centers of the fundamental bands should differ in frequency by 825 cm^{-1} ; for H^{35}Cl the frequency of the origin is 2885.9 cm^{-1} , and hence for D^{35}Cl it should be 2061 cm^{-1} , in good agreement with the observed value. In this particular case the isotopic shift is so large that the two vibration-rotation bands do not overlap as they do for H^{35}Cl and H^{37}Cl . The bands for the two isotopic molecules H^{35}Cl and D^{35}Cl are actually quite separate from one another.

ELECTRONIC SPECTRA

30a. Structure of Electronic Bands.—As has been already stated, the spectra of molecules observed in the visible and ultra-violet regions are due to a transition from one electronic state to another. The vibrational changes that accompany the electronic transition are responsible for the various bands, their fine structures being due to the associated changes in rotational energy. To a close approximation, the total energy E of a molecule may be regarded as made up of the electronic energy E_e , the vibrational energy E_v , and the rotational energy E_r ; thus,

$$E = E_e + E_v + E_r. \quad (30.1)$$

The vibrational energy may be expressed by means of equation (29.11), viz.,

$$E_v = (v + \frac{1}{2})hc\omega - (v + \frac{1}{2})^2hc x\omega + (v + \frac{1}{2})^3hcy\omega + \dots, \quad (30.2)$$

where the equilibrium vibration frequency ω (the subscript e has been

omitted for simplicity) and the anharmonicity constants x, y , etc., refer to the values in the particular electronic state being considered; these will vary from one level to another. The employment of the appropriate values for ω, x, y , etc., virtually takes into account the interaction between electronic and vibrational energy states. Similarly, the use of equation (29.26), i.e.,

$$E_r = B_v J(J+1)hc - D_v J^2(J+1)^2hc + \dots, \quad (30.3)$$

for the rotational energy, allows for vibrational and rotational interactions; in this expression B_v and D_v , defined by equations (29.31) and (29.32), depend on the particular vibrational level and electronic state of the molecule. In a sense, therefore, equation (30.3) takes into account electronic and rotational interactions; there are, however, certain other effects which will be considered later (Section 30e).

If the rotational transition is disregarded provisionally, or, in other words, the rotational energy change is taken as zero, the energy change accompanying an electronic transition will be given by

$$E' - E'' = (E'_e - E''_e) + (E'_v - E''_v). \quad (30.4)$$

The expression for the frequency of the corresponding spectrum is then

$$\nu_0 = \nu_e + \left\{ (v' + \frac{1}{2})\omega' - (v' + \frac{1}{2})^2 x' \omega' + \dots \right\} - \left\{ (v'' + \frac{1}{2})\omega'' - (v'' + \frac{1}{2})^2 x'' \omega'' + \dots \right\}, \quad (30.5)$$

where ν_e is written for $(E'_e - E''_e)/hc$; the vibrational quantum numbers in the final and initial states are v' and v'' , respectively; ω' and ω'' are the equilibrium vibration frequencies of the molecule in these states, and x' and x'' are the corresponding anharmonicity constants. Since the rotational energy change has been assumed to be zero, equation (30.5) gives the frequencies ν_0 of the centers (or origins) of the series of vibrational bands making up the electronic spectrum.

Because of the electronic transition there is no restriction as to the change in the vibrational quantum number; that is to say, there is no restriction as to the value of Δv (cf. Section 32e). Although certain values are preferred, Δv may have almost any positive or negative integral value, or it may be zero. Electronic transitions in which the vibrational quantum number changes by as much as ten are not uncommon. It follows, therefore, that a large number of bands are generally observed in the band system of any molecule. For convenience in classification, a series of bands having a constant value of $v' - v''$ is called a *sequence*, and the term *progression* is used to describe a set of bands having a definite value of either v' or v'' , while the other varies regularly, e.g., v' equals 0, while v'' equals 0, 1, 2, etc.

It is of interest to note that in absorption the electronic spectrum generally consists of a single progression only, with v'' equal to zero. The reason for this is not difficult to understand. At ordinary temperatures most molecules are in their lowest ($v = 0$) vibrational levels of the electronic

ground state. When the molecules absorb enough energy to reach a higher electronic level, there is no restriction as to the vibrational quantum number v' in the upper state, but that in the lower state, i.e., v'' , is zero for nearly all the molecules in the system. The band group will thus consist almost exclusively of the progression for which v'' is zero. If the temperature of the gas is high, or the vibrational quantum is small, i.e., the equilibrium vibration frequency of the molecule is small, an appreciable number of molecules in the ground state will be in the $v = 1$ level. In these circumstances, the progression $v'' = 1$ will appear in the absorption spectrum, in addition to the $v'' = 0$ progression. The relative simplicity of electronic absorption spectra is of great assistance in the elucidation of the more complex emission spectra, when v' and v'' can both have almost any value within reason.

If ν_{00} is the frequency of the origin of the band for the transition $v' = 0$ to $v'' = 0$, then it is seen from equation (30.5) that

$$\nu_{00} = \nu_e + (\tfrac{1}{2}\omega' - \tfrac{1}{4}x'\omega' + \dots) - (\tfrac{1}{2}\omega'' - \tfrac{1}{4}x''\omega'' + \dots). \quad (30.6)$$

Upon introducing this result, equation (30.5) may be written in the form

$$\begin{aligned} \nu_0 &= \nu_{00} + \{(1 - x')\omega' - v'x'\omega' + \dots\}v' \\ &\quad - \{(1 - x'')\omega'' - v''x''\omega'' + \dots\}v'' \quad (30.7) \\ &= \nu_{00} + (a' - b'v' + \dots)v' - (a'' - b''v'' + \dots)v'', \end{aligned}$$

where a has been written for $(1 - x)\omega$ and b for $x\omega$. An expression of the form of equation (30.7) has been frequently used in spectroscopy to represent the frequencies of the origins of the band systems corresponding to a particular electronic transition. For example, carbon monoxide exhibits an electronic band spectrum in the range of 1300 Å to 2700 Å, generally known as the *fourth positive group* of carbon monoxide. The frequencies of the origins of the bands are expressed with considerable accuracy by the equation

$$\begin{aligned} \nu_0 &= 64,746.5 + (1498.36 - 17.2505v' + \dots)v' \\ &\quad - (2156.05 - 13.2600v'' + \dots)v'', \end{aligned}$$

and so the values of a' , b' and a'' , b'' are immediately known. Since b is equivalent to $x\omega$ and a to $(1 - x)\omega$, it is possible to derive the equilibrium vibration frequencies of the carbon monoxide molecule in the two electronic states. The values are found to be 1515.61 and 2169.31 cm^{-1} ; the former refers to the excited state of the molecule and the latter to the ground state. From the frequency, the force constant for carbon monoxide in its normal state can be calculated by means of equation (29.47); the result is 19.01×10^6 dynes per cm. This exceptionally high value is in harmony with the generally accepted structure of carbon monoxide as involving resonance between double and triple bonded forms.

According to the expression recorded above, the value of ν_{00} for the fourth positive group of carbon monoxide is 64,746.5 cm^{-1} , and since ω' , $x'\omega'$, ω''

and $x''\omega''$ are known, as seen above, it is possible to calculate ν_0 for the given electronic transition by means of equation (30.6). The result in this particular case is $65,074.3 \text{ cm.}^{-1}$, which is equivalent to an energy of 8.06 e.v.

It is important to recall that because there is always a change of electric dipole moment accompanying an electronic transition, even homopolar molecules, such as hydrogen, oxygen, nitrogen, etc., exhibit electronic band spectra. These spectra provide a method by means of which information, such as that just derived for carbon monoxide, concerning equilibrium vibration frequencies and force constants of symmetrical diatomic molecules can be obtained. It will be seen later that Raman spectra serve as another means, although less accurate, for providing the same data.

30b. Rotational Fine Structure.—The possibility of rotational energy changes accompanying each vibrational transition accounts for the fine structure of the bands. If the rotational energy, as defined by equation (30.3) is added to the electronic and vibrational energies, then it can be readily shown, by the same methods as were used in Section 29, that the frequencies of the rotational lines constituting the *P*, *Q* and *R* branches of any band are given by equations exactly analogous to (29.35), (29.37) and (29.36), respectively; they are

$$J - 1 \rightarrow J: \quad \nu(P) = \nu_0 - (B' + B'')J + (B' - B'')J^2 + \dots \quad (30.8)$$

$$J \rightarrow J: \quad \nu(Q) = \nu_0 + (B' - B'')J + (B' - B'')J^2 + \dots \quad (30.9)$$

$$J \rightarrow J + 1: \quad \nu(R) = \nu_0 + (B' + B'')J + (B' - B'')J^2 + \dots \quad (30.10)$$

where ν_0 is the frequency of the origin of the particular band, as represented by the equations in Section 30a. It should be noted that B' and B'' now refer to different electronic states as well as, generally, to different vibrational states, and so they are usually appreciably different from one another. In deriving equations (30.8), (30.9) and (30.10), the selection rule $\Delta J = +1, 0$ and -1 has been used for the *P*, *Q* and *R* branch, respectively. If the total electronic angular momentum of the molecule (Λ) is zero in both upper and lower states taking part in the electronic transition, that is, both are Σ states, then the only rotational changes permitted are those with ΔJ equal to $+1$ or -1 ; hence in such ($\Sigma \leftrightarrow \Sigma$) transitions *P* and *R* branches only are observed. If, however, Λ differs from zero in either or both of the electronic states, ΔJ can be zero, as well as ± 1 , and so the *Q* branch is possible, in addition to *P* and *R* branches.

From an analysis of the rotational structure of the bands in an electronic spectrum it is thus possible to evaluate the equilibrium rotational constants B'_e and B''_e from which the moments of inertia, and hence the equilibrium internuclear distances, of the molecule can be calculated in the upper and lower electronic states. The information obtained in this manner is particularly useful in connection with homopolar diatomic molecules which, as already seen, do not yield either vibration-rotation or pure rotation spectra. Attention should be called to the fact that the spacing of the

rotational lines in the electronic band spectra of symmetrical molecules presents a special problem which will be considered in Section 31.

30c. Band Heads.—Examination of a band group shows that each vibrational band is usually sharply defined at one end, the so-called *head* of the band, and is more diffuse or shaded at the other end. The band is said to be *degraded* in the diffuse direction; if this part of the band is in the direction of higher frequency (lower wave lengths) than the head, it is said to be degraded toward the violet. On the other hand, if the band is sharp at the higher frequency end, but shaded in the lower frequency direction, it is degraded towards the red. As a general rule, all the bands in a given group are degraded in the same direction.

Although band heads are very useful for identification purposes, they have no special theoretical significance. They owe their origin to the fact that the rotational lines are crowded together in its vicinity, while they are spaced further apart towards the degraded end of the band. These characteristics of a vibrational band can be understood from a consideration of the general equation for the rotational fine structure. The equations (30.8) and (30.10) for the frequencies of the *P* and *R* branches may be written in the form

$$\nu = \nu_0 + (B' + B'')m + (B' - B'')m^2 + \dots, \quad (30.11)$$

where m can be $\pm 1, \pm 2, \pm 3$, etc.; for the *P* branch m has the negative values, while for the *R* branch it has the positive values. The factor $B' - B''$ may be positive or negative, according as B' is greater than B'' or B' is less than B'' , respectively; this may vary from one band to another, but the sign is generally the same, even though the value may alter slightly, for all the bands making up a given group. The reason for this fact is that B_0 is determined largely by the moment of inertia of the molecule in the particular electronic state, the value of ν , the vibrational quantum number, having only a secondary influence. Hence, the values of B' and B'' , and consequently of $B' - B''$, will depend primarily on the two electronic states responsible for the spectrum. Its sign, at least, will be the same for a given band group, even if its value alters somewhat from one band to another.

Consider the case in which $B' - B''$ is negative; then as m increases in the series $+1, +2, +3$, etc., that is, in the *R* branch, the value of ν increases at first, since $B' + B''$ is numerically greater than $B' - B''$. However, $(B' - B'')m^2$ changes at a more rapid rate than does $(B' + B'')m$, and so the frequency spacing between successive lines gradually decreases and the lines begin to crowd together. At a certain value of m the frequency increase due to the term $(B' + B'')m$ becomes numerically equal to the decrease resulting from the negative term $(B' - B'')m^2$; this occurs at the band head. For higher values of m the frequencies of successive lines now form a decreasing series, with spacings becoming increasingly larger. In other words, the successive lines begin to turn back upon themselves and continue toward the lower frequency region. It is obvious that in the vicinity of the point at which the reversal occurs the rotational lines crowd together, thus pro-

ducing the sharply defined termination characteristic of the band head. In the P branch of the same band, both terms $(B' + B'')m$ and $(B' - B'')m^2$ will be negative, since m has a series of negative values, while m^2 is always positive. It follows, therefore, that the frequencies of the lines of the P branch will become successively smaller, and the separation of consecutive lines will become larger as m increases numerically. At the same time, as is the case in all band spectra, the intensity of the lines diminishes, and so the band will shade off gradually on the low frequency side. It is clear, therefore, that when $B' - B''$ is negative, the band will be degraded toward the red end of the spectrum.

By means of arguments similar to those employed in the preceding paragraph, it can be shown that if $B' - B''$ is positive, the R branch of the band, with positive m values, will be degraded toward the region of higher frequency, that is, toward the violet. At the same time, it can be seen that in the P branch the lines crowd together to form a head at the red end of the band.

In general, the change of frequency with increasing numerical value of m is zero at the band head; the value of m at this point can therefore be obtained if equation (30.11) is differentiated with respect to m , and the result equated to zero; hence it follows that

$$m_{\text{head}} = - \frac{B' + B''}{2(B' - B'')} \quad (30.12)$$

If $B' - B''$ is positive, then m_{head} will be negative, so that the head will be found in the P branch; on the other hand, if $B' - B''$ is negative, m will be positive and the head will form in the R branch. These results are in harmony with the conclusions reached previously. If $B' - B''$ is small numerically, m_{head} will be very large; under these conditions it may not be possible to observe the band head, because of the falling off in the intensity of the lines for large values of m .

It may be remarked, in passing, that a band head is to be expected, theoretically, in ordinary vibration-rotation and pure rotation spectra in the infra-red. In these cases, however, the moments of inertia are not very different in the two states involved in the transition, so that $B' - B''$ is very small. As just seen, the head of the band would appear only at large (numerical) values of m , but the intensity of the lines is then so feeble as to render them, and consequently the band head, undetectable.

The frequencies of the lines in the Q branch are represented by

$$\nu = \nu_0 + (B' - B'')J + (B' - B'')J^2 + \dots,$$

in which J may be a positive integer or zero. Since $B' - B''$ is relatively small, the lines constituting the Q branch will be relatively close together, but they will always proceed in one direction or another, depending on whether $B' - B''$ is positive or negative. If $B' - B''$ is very small, the lines for low values of J will be close together, but they will separate out for

higher J values. In this case the band gives the appearance of possessing a head in the Q branch, in addition to the head that may be present in the P or R branch.

30d. Isotope Effect in Electronic Spectra.—If ω_1 and ω_2 are the equilibrium vibration frequencies of the two isotopic forms of a given molecular species in the same electronic state, then ω_2 is equal to $\rho\omega_1$, where ρ is defined by $(\mu_1/\mu_2)^{1/2}$, as shown in Section 29h. By utilizing two equations of the form of (30.5), one for each isotopic molecule, to give ν_0 , the frequency of the origin of any band in a particular group, it is possible to derive an equation for the isotopic shift. Because of the anharmonicity terms, the resulting expression is not simple, but the general nature of the conclusions can be arrived at, with sufficient accuracy, by making the approximation of harmonic oscillation. It is then possible to write for one isotope

$${}_1\nu_0 = \nu_e + (v' + \tfrac{1}{2})\omega'_1 - (v'' + \tfrac{1}{2})\omega''_1 \quad (30.13)$$

and for the other isotope,

$${}_2\nu_0 = \nu_e + (v' + \tfrac{1}{2})\omega'_2 - (v'' + \tfrac{1}{2})\omega''_2 \quad (30.14)$$

for the frequencies of the origins of corresponding bands, i.e., involving the same transition, $v'' \rightarrow v'$. Subtraction of equations (30.13) and (30.14) gives the isotopic shift $\Delta\nu_i$ as

$$\Delta\nu_i = (\omega'_1 - \omega'_2)(v' + \tfrac{1}{2}) - (\omega''_1 - \omega''_2)(v'' + \tfrac{1}{2}),$$

assuming, as is very probable, that the frequency ν_e , representing the electronic energy change, is the same for both isotopic molecules. Upon introducing the relationship $\omega_2 = \rho\omega_1$, which will apply to both electronic states, it follows that

$$\Delta\nu_i = (1 - \rho)\{\omega'_1(v' + \tfrac{1}{2}) - \omega''_1(v'' + \tfrac{1}{2})\}. \quad (30.15)$$

As mentioned in Section 29h, the isotopic shift is greater the larger the ratio of the reduced masses of the two isotopic forms; it is, therefore, most readily observed with molecules containing atoms of low atomic weight.

The electronic spectrum of oxygen provided the first case of the detection of a new isotope as a consequence of the shift of the center of a vibrational band. It had been noted that in the so-called A band in the spectrum of molecular oxygen, which involves a transition from $v' = 0$ to $v'' = 0$, there appeared a faint A' band. The latter was an almost exact duplicate of the A band, although it actually contained twice the number of rotational lines. The suggestion was made that the strong A band was due to $^{16}\text{O}^{16}\text{O}$, and that the corresponding, weak, A' band was produced by $^{16}\text{O}^{18}\text{O}$ molecules. If both v' and v'' in equation (30.15) are set equal to zero, which is the condition for the A band, the result should give the isotopic shift for this band; this is

$$\Delta\nu_i = \tfrac{1}{2}(1 - \rho)(\omega'_1 - \omega''_1). \quad (30.16)$$

The values of ω'_1 and ω''_1 , for the common isotopic form $^{16}\text{O}^{16}\text{O}$, are known accurately from an examination of the electronic band group containing the A band; the difference $\omega'_1 - \omega''_1$ is -150.35 cm.^{-1} , and if ρ is determined from the presumed atomic weights, 16 and 18, respectively, of the isotopic atoms, it is found that $\Delta\nu_i$, according to equation (30.16), should be -2.053 cm.^{-1} . If the view expressed above that the A band is due to $^{16}\text{O}^{16}\text{O}$ and the A' band to $^{16}\text{O}^{18}\text{O}$ is correct, the frequency separation of the origins of the bands should have this value; the observed separation is -2.067 cm.^{-1} , the small discrepancy being due to the neglect of anharmonicity in the foregoing calculations. If proper allowance is made for the deviation from simple harmonic motion, the agreement is almost perfect. The experimental results may therefore be regarded as establishing the existence of an isotope of oxygen with a mass number of 18.

The isotopic shift in the rotational lines will be given by an expression which is similar to that applicable to vibration-rotation and pure rotation bands [equation (28.17)]. Thus, if the moments of inertia are taken to be the same in both upper and lower electronic states, which is not strictly true, the frequency change for corresponding rotational lines is given by

$$\Delta\nu_i = 2BJ(1 - \rho^2).$$

For the isotopic forms of molecular oxygen just considered, this becomes

$$\begin{aligned}\Delta\nu_i &= 0.01112BJ \\ &= 0.01605J,\end{aligned}$$

and hence the shift should be quite noticeable for lines that are some distance from the center of the band. The experimental results are in excellent accord with these derived theoretically. Incidentally, it may be mentioned that the presence of twice as many rotational lines in the A' band as in the A band of oxygen, is in agreement with the fact that the $^{16}\text{O}^{18}\text{O}$ molecule is unsymmetrical whereas $^{16}\text{O}^{16}\text{O}$ is symmetrical (see Section 31d).

In addition to the oxygen isotope of mass 18, the third isotopic form of oxygen, with a mass number of 17, was discovered by means of electronic spectra; so also were the ^{13}C isotope of carbon and the ^{15}N isotope of nitrogen.

30e. Interaction of Electronic and Rotational Energies.—No attention has been paid so far to the possibility of coupling of rotational and electronic motions; this omission has not been significant since the diatomic molecules have been tacitly assumed to be in $^1\Sigma$ states. In such states, the resultant electron spin S , and the resultant orbital angular momentum Λ of the electrons are both zero (see Section 2d); the total angular momentum of the molecule is then simply due to the rotation of the nuclei, and hence is determined by the rotational quantum number J only. In other cases, there is the possibility of some form of coupling between the rotation of the molecule and the electronic motion which has a significant effect on the rotational levels. Five different modes of coupling have been distinguished, but only two, Hund's cases (a) and (b), are of common occurrence. It should be

higher J values. In this case the band gives the appearance of possessing a head in the Q branch, in addition to the head that may be present in the P or R branch.

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assuming, as is very probable, that the frequency ν_e , representing the electronic energy change, is the same for both isotopic molecules. Upon introducing the relationship $\omega_2 = \rho\omega_1$, which will apply to both electronic states, it follows that

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For the isotopic forms of molecular oxygen just considered, this becomes

$$\begin{aligned}\Delta\nu_i &= 0.01112BJ \\ &= 0.01605J,\end{aligned}$$

and hence the shift should be quite noticeable for lines that are some distance from the center of the band. The experimental results are in excellent accord with these derived theoretically. Incidentally, it may be mentioned that the presence of twice as many rotational lines in the A' band as in the A band of oxygen, is in agreement with the fact that the $^{16}\text{O}^{18}\text{O}$ molecule is unsymmetrical whereas $^{16}\text{O}^{16}\text{O}$ is symmetrical (see Section 31d).

In addition to the oxygen isotope of mass 18, the third isotopic form of oxygen, with a mass number of 17, was discovered by means of electronic spectra; so also were the ^{13}C isotope of carbon and the ^{15}N isotope of nitrogen.

30e. Interaction of Electronic and Rotational Energies.—No attention has been paid so far to the possibility of coupling of rotational and electronic motions; this omission has not been significant since the diatomic molecules have been tacitly assumed to be in $^1\Sigma$ states. In such states, the resultant electron spin S , and the resultant orbital angular momentum Λ of the electrons are both zero (see Section 2d); the total angular momentum of the molecule is then simply due to the rotation of the nuclei, and hence is determined by the rotational quantum number J only. In other cases, there is the possibility of some form of coupling between the rotation of the molecule and the electronic motion which has a significant effect on the rotational levels. Five different modes of coupling have been distinguished, but only two, Hund's cases (a) and (b), are of common occurrence. It should be

emphasized that these cases represent limiting ideal behavior, which are often good approximations; intermediate cases are, however, sometimes observed.

Case (a): In this case the interaction of rotation and electronic (orbital) motion is supposed to be very weak, but the latter is very strongly coupled to the line joining the nuclei. The total electronic angular momentum Ω about the internuclear axis, obtained by adding Λ and Σ (see Section 2c), is well defined and forms a resultant J by combining with the rotational motion. It follows, therefore, that J cannot be less than Ω , and the former has the possible values

$$J = \Omega, \Omega + 1, \Omega + 2, \dots, \quad (30.17)$$

and levels with J less than Ω do not occur. Since Ω involves the spin quantum number Σ , both Ω and J will be integral if the molecule contains an even number of electrons, but it will be an odd number of half integers if the number of electrons in the molecule is odd. The rotational energy is now given, as a first approximation, by the expression

$$E_r = B_v \{J(J + 1) - \Omega^2\} hc, \quad (30.18)$$

but since more than one value of Ω , which is equal to $|\Lambda + \Sigma|$ is possible, there will be a number of values E_r for each value of J . In other words, there will be several sets of rotational levels, the number of sets depending on the possible Ω values. In each set, the levels for which J is less than Ω will be missing, as indicated above. It will be observed that in $^1\Sigma$ states, Ω is zero and hence equation (30.18) reduces to the form employed in the earlier parts of this chapter. For such molecules, therefore, there is but one set of rotational levels, as has been assumed hitherto.

An example of case (a) coupling is found in the ground state of nitric oxide; here Λ is equal to 1, and S is $\frac{1}{2}$, so that the state may be described by the symbol $^2\Pi$. The possible values of Σ are $+\frac{1}{2}$ and $-\frac{1}{2}$, and consequently Ω can be $\frac{1}{2}$ or $\frac{3}{2}$; there are thus two sets of rotational levels with somewhat different energies. In the first, designated by $^2\Pi_{1/2}$, the smallest value of J is $\frac{1}{2}$, and subsequent values are $\frac{3}{2}$, $\frac{5}{2}$, $\frac{7}{2}$, etc.; in the second set, represented by the term symbol $^2\Pi_{3/2}$, the lowest value of J is $\frac{3}{2}$, and this is followed by $\frac{5}{2}$, $\frac{7}{2}$, etc.

As a more complicated illustration, there may be taken the hypothetical case of a molecule for which Λ is 2, and S is 1, so that it is in a $^3\Delta$ state. The possible values of Σ are 1, 0 and -1 , and those of Ω are 3, 2 and 1. There are thus three sets of rotational lines, represented by $^3\Delta_1$, $^3\Delta_2$ and $^3\Delta_3$, respectively; in the first the $J = 0$ level is missing, in the second the first two levels, $J = 0$ and 1, are missing, and in the third set the levels with $J = 0, 1$ and 2 are absent. The $J = 0$ line is thus completely missing, the $J = 1$ line is a singlet, $J = 2$ is a doublet, while the others are all triplets.

Case (b): When Λ is zero and S differs from zero, that is, in states other than $^1\Sigma$, and also in certain cases when Λ is not zero, the spin may be only

weakly coupled to the internuclear axis. In these circumstances, Ω is not defined, and so the orbital angular momentum Λ couples with the rotation to give a resultant K , representing the total angular momentum apart from spin. The possible K values are

$$K = \Lambda, \Lambda + 1, \Lambda + 2, \dots, \quad (30.19)$$

and hence for Σ states, when Λ is zero, K can be 0, 1, 2, etc. The quantum number K combines with the total spin S to give the resultant J , for the total angular momentum including electron spin. The possible values of J for a given K are determined by the familiar principle of vector addition in quantum theory, so that

$$J = K + S, K + S - 1, K + S - 2, \dots, |K - S|. \quad (30.20)$$

Thus, in general, except when K is less than S , each level with a given value of K consists of $2S + 1$ components; that is to say, each rotational level has a multiplicity of $2S + 1$. As a result of the coupling between K and S these multiplets have slightly different energies, the splitting increasing as K increases. It will be noted from equation (30.20) that since K is integral, while S is integral or half-integral according as to the number of electrons is even or odd, the value of J will be integral or half-integral, respectively.

The best known instances of case (*b*) coupling occur in $^2\Sigma$ and $^3\Sigma$ states; the latter is particularly interesting as the ground state of molecular oxygen is $^3\Sigma$. For this substance the spin component Σ is zero and S is 1, so that the possible values of K and J are

$$K = 0, 1, 2, \dots$$

and

$$J = K + 1, K \quad \text{and} \quad K - 1.$$

Although it might appear that for $K = 0$ there should be two values of J , actually only one is possible, since the smallest value of J is $|K - S|$, as seen from equation (30.20), and this will be unity. The lowest rotational level, for $K = 0$, is thus a singlet. In general, for case (*b*) coupling, the level for which K is zero is a singlet with J equal to S . For all other K values, viz., 1, 2, 3, etc., there are three values of J , so that each of the rotational lines is a triplet. The $^{16}\text{O}^{16}\text{O}$ molecule presents a special case as it is a homonuclear molecule and hence alternate rotational lines are missing (cf. Section 31d).

30f. Λ -type Doubling.—It was mentioned near the end of Chapter I (Section 2a) that when the orbital angular momentum Λ is not zero, that is to say, in all except Σ states, each state is doubly degenerate. This is because the two levels for which Λ is equal to $+L$ and $-L$ have identical energies. On account of interaction between the electronic and rotational motions, however, the levels are separated and each rotational line in Π and Δ states is split into two components; this effect is known as *Λ -type doubling*. The separation of the rotational doublets is quite small for low values of

the resultant quantum number J , but it becomes more marked as J increases, although it is never very appreciable. The occurrence of Λ -type doubling may be illustrated by reference to nitric oxide; as already seen, this has a normal $^2\Pi$ state, the components being $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$. As a result of Λ -type doubling, each of the rotational levels in both states is a doublet, so that there are, in effect, two levels for $J = \frac{1}{2}$ and four levels for $J = \frac{3}{2}, \frac{5}{2}$, etc.

MOLECULAR SYMMETRY EFFECTS

31a. Symmetry Properties and Rotational States.—The symmetry properties of molecules have an important influence on the rotational energy levels, with results of interest both in spectroscopy and in chemistry. Since the great majority of diatomic molecules in their normal (ground) states are in $^1\Sigma$ states, the discussion will at first be restricted to molecules of this type. For any diatomic molecule and, in fact, for any linear molecule, any plane passing through the line joining the nuclei is a plane of symmetry of the molecule. Because of the existence of this symmetry element, it is possible to characterize the electronic eigenfunction of a molecule as *positive* or *negative* (cf. Section 2e). By the methods of quantum mechanics, it has been shown that the electronic (orbital) eigenfunction of a system with cylindrical symmetry, such as any diatomic or linear molecule whose nuclei may be regarded as fixed, can be represented by (cf. Section 13g for central force field)

$$\psi_e = \Phi e^{i\Lambda\phi}, \quad (31.1)$$

where Λ has the same significance as before, and ϕ is the azimuthal angle of one of the electrons about the line joining the nuclei, starting from a fixed reference plane; Φ is a function of the other coordinates, including the azimuthal angles of the other electrons relative to the one chosen for the frame of reference. For Σ states, the quantum number Λ is zero; the factor $e^{i\Lambda\phi}$ is then unity, and the eigenfunction ψ_e depends on the relative azimuths ϕ_{12} of the various electrons which appear in the function Φ . On reflecting the eigenfunction at a plane passing through the nuclei, the angles ϕ_{12} become $-\phi_{12}$. Hence, if the function Φ contains terms such as $\sin \phi_{12}$, it is evident that it, and consequently ψ_e , will change sign, i.e., it is antisymmetric, for reflection through the internuclear plane. On the other hand, ψ_e will remain unchanged, i.e., it is symmetric, if Φ contains such terms as $\cos \phi_{12}$, $\sin^2 \phi_{12}$ or $\cos^2 \phi_{12}$. Electronic eigenfunctions of the former type belong to negative (Σ^-) states, while the latter correspond to positive (Σ^+) states.

It may be remarked that reflection of the diatomic molecule through the origin, that is, inversion of both electrons and nuclei, employing the term *inversion* in the crystallographic sense, is equivalent to reflection of the electrons only in the internuclear plane. Hence positive and negative states of a diatomic molecule may be defined, alternatively, as those for which inversion of electrons and nuclei leaves the sign of the electronic eigenfunction unchanged or changed in sign, respectively.

The foregoing discussion has referred specifically to the electronic (orbital) eigenfunction of the diatomic or linear molecule; it is now necessary to consider the symmetry properties of the vibrational and rotational wave functions. The vibrational function is unaffected by any symmetry operations, for it depends only on the internuclear distance, and this remains unchanged. With the rotational function, however, the case is different. It is evident from the results in Section 9d that the eigenfunction for a linear rotator will possess symmetry properties, since it depends on the azimuthal angle. Evaluation of the eigenfunctions for different values of the rotational quantum number (J or K) shows that it remains unchanged upon reflection at the origin, i.e., inversion, of the molecule, including the nuclei, when J (or K , for case (b)) is even but it changes sign when J (or K) is odd.

Neglecting the nuclear spin contribution, for the present, the complete eigenfunction ψ of a molecule may be written as the product of the electronic (ψ_e), the vibrational (ψ_v), and the rotational (ψ_r) functions, so that

$$\psi = \psi_e \psi_v \psi_r. \quad (31.2)$$

As already seen, for Σ^+ states the function ψ_e remains unchanged upon inversion of the electrons and nuclei; further, ψ_v is unaffected, in any event, and ψ_r is unaltered if the rotational quantum number is even. It follows, therefore, that the complete eigenfunction ψ for a Σ^+ state is unchanged upon inversion for even values of the rotational quantum number. The rotational levels in a Σ^+ state with even values of J (or K for case (b), coupling) are thus called *positive rotational levels*; for odd values of J (or K), they are *negative rotational levels*. By means of exactly similar arguments, it can be shown that for Σ^- states, the odd rotational levels are positive, while the even rotational levels are negative. The results may, therefore, be summarized as follows:

	Σ^+ states	Σ^- states
	Rotational Levels	
J (or K) = 0, 2, 4, ...	Positive	Negative
J (or K) = 1, 3, 5, ...	Negative	Positive

It may be remarked that the positive and negative character of rotational levels is also evident in Π and Δ states; it appears from quantum mechanics that in every Λ -type rotational doublet one level is positive while the other is negative. That is to say, in these states there is a positive and negative rotational level for each value of J (or K). These levels are found to alternate, so that if the lower level of one doublet is positive, the corresponding level of the next doublet will be negative.

31b. Odd and Even Electronic States.—If, in addition to being linear, the nuclei of a diatomic molecule have equal charges, e.g., H_2 or HD , then g and u character is possible, as mentioned in Section 2e. If the orbital wave function of the electronic system is $\psi_e(x, y, z)$, then reflection of the electrons at the center of symmetry, i.e., inversion of the electrons only, will

change the coordinates x, y, z of all the electrons to $-x, -y, -z$; the electronic eigenfunction then becomes $\psi_e(-x, -y, -z)$. Since the molecule is symmetrical, as far as the nuclear charges are concerned, it is evident that inversion of the coordinates of the electrons will leave the potential energy of the system unchanged. Hence, for a given eigenvalue E of the total energy, both orbital functions $\psi_e(x, y, z)$ and $\psi_e(-x, -y, -z)$ must be satisfactory solutions of the wave equation for the system; further, linear combinations of these two functions, such as

$$\Psi_g = \psi_e(x, y, z) + \psi_e(-x, -y, -z) \quad (31.3)$$

and

$$\Psi_u = \psi_e(x, y, z) - \psi_e(-x, -y, -z), \quad (31.4)$$

will also be acceptable solutions. It can be seen that of these solutions, the one designated Ψ_g remains unchanged when the electron coordinates are inverted, i.e., when x, y, z are changed to $-x, -y, -z$, and vice versa; hence it has the characteristics of an *even* (g) state. On the other hand, the solution Ψ_u changes sign upon inversion of the coordinates of the electrons, and so it represents an *odd* (u) state.

In the case just considered, the system would be degenerate, for the two eigenfunctions Ψ_g and Ψ_u would correspond to states of the same energy. If the system is not degenerate, however, one of the solutions would be zero: if Ψ_g were zero, then

$$\psi_e(x, y, z) = -\psi_e(-x, -y, -z),$$

so that the eigenfunction changes sign upon inversion of the coordinates of the electrons; the system is consequently in a u state. On the other hand, if Ψ_u were zero,

$$\psi_e(x, y, z) = \psi_e(-x, -y, -z),$$

and the eigenfunction does not change sign upon inversion; the system is thus in a g state. It follows, therefore, that for a nondegenerate state of a homonuclear molecule, the orbital eigenfunction must already have g or u character. If the system is doubly degenerate, however, the two solutions of the wave equation corresponding to the given eigenvalue for the energy will be g and u , respectively. It appears that in actual practice there is no even-odd degeneracy, and so the orbital wave function of the electrons for a homonuclear molecule must automatically represent either a g or a u state. Attention may be called to the fact that the g and u character is evident, to some extent, even when the two nuclei are not equally charged, provided they are closely similar; this is the case, for example, with the diatomic CN radical.

31c. Symmetric and Antisymmetric Rotational Levels.—For homonuclear molecules, that is, molecules whose nuclei are *identical*, e.g., H_2 but not HD, there still remains to be considered the result of another symmetry operation, namely exchange of the identical nuclei. This operation is equivalent to two others, for which the results are already known. These

are, first, inversion of all the particles, both the electrons and nuclei, which determines the positive or negative character, followed by re-inversion of the electrons only, upon which the g or u property depends. It is obvious that for a molecule in a positive electronic state and having also the g property of the electrons, exchange of the nuclei will leave the electronic eigenfunction unchanged; such a wave function is said to be *symmetric in the nuclei*. On the other hand, if the positive state is associated with the u property of the electrons, the sign of the eigenfunction will be reversed; the wave function is then *antisymmetric in the nuclei*. The results for molecules in negative states can be readily derived in the same manner, and the conclusions reached for various combinations are summarized below.

$$\begin{array}{lll} \Sigma_g^+ & \text{and} & \Sigma_u^-: \text{symmetric in the nuclei} \\ \Sigma_g^- & \text{and} & \Sigma_u^+: \text{antisymmetric in the nuclei.} \end{array}$$

The property of being symmetric or antisymmetric in the nuclei is also applicable to the rotational eigenfunctions which, as already seen, have positive and negative character. Just as a positive electronic state combined with g character gives an orbital function that is symmetric in the nuclei, so combination of a positive rotational level with g character of the electrons, corresponds to a rotational state that is symmetric in the nuclei. By analogy with the results given above, the general conclusions are as follows:

$$\begin{array}{lll} \overset{+}{g} & \text{and} & \bar{u}: \text{symmetric} \quad (s) \\ \bar{g} & \text{and} & \overset{+}{u}: \text{antisymmetric} \quad (a) \end{array}$$

where the $+$ and $-$ signs now refer to the rotational levels. Combination of these facts with those recorded in Section 31a concerning the connection between positive and negative rotational levels and the values of J (or K), in g and u electronic states, gives the results quoted in Table XI for the

TABLE XI. SYMMETRIC AND ANTISYMMETRIC CHARACTER OF ROTATIONAL LEVELS

J	Σ_g^+	Σ_g^-	Σ_u^+	Σ_u^-
0	$+s$	$-a$	$+a$	$-s$
1	$-a$	$+s$	$-s$	$+a$
2	$+s$	$-a$	$+a$	$-s$
3	$-a$	$+s$	$-s$	$+a$
4	$+s$	$-a$	$+a$	$-s$
5	$-a$	$+s$	$-s$	$+a$

symmetric and antisymmetric character of rotational levels in the four types of Σ states of a homonuclear molecule. If the molecule exhibits Hund's case (b) coupling, as does the $^{16}\text{O}^{16}\text{O}$ molecule, the characters are similar to those in Table XI, except that K , as defined by equation (30.19), replaces the quantum number J .

The situation is analogous with homonuclear molecules in Π and Δ states; the general rule that $\overset{+}{g}$ and \bar{u} rotational levels are symmetric, while \bar{g} and $\overset{+}{u}$ levels are antisymmetric, is still applicable. However, as seen above

(Section 31a), each rotational level has a positive and a negative component, and hence one component of every rotational level is symmetric while the other is antisymmetric.

31d. Selection Rules for Rotational Levels.—As shown in Section 27d, the probability of transition from one state to another, under the influence of dipole radiation, depends on the matrix element P_{mn} , of which the x component is given by equation (27.2), viz.,

$$P_{mn(x)} = \int \psi_m^* (\sum_j \epsilon_j x_j) \psi_n d\tau. \quad (31.5)$$

If both the rotational levels involved in a transition are positive, reflection of the rotational eigenfunction at the origin, will leave unchanged the signs of ψ_m^* and ψ_n , for the two combining levels. However, the sign of the x coordinates will be reversed, and so the sign of the integrand as a whole will be reversed. The value of a definite integral must be independent of any transformation of the coordinates, and so it is evident that the integral in equation (31.5), and hence the x component of the matrix element P_{mn} must be zero. The same considerations apply to the y and z components, and so the transition probability between two positive rotational levels is zero; the transition is thus forbidden. In the same way it can be shown that transitions between two negative levels is also forbidden. For a rotational transition between a positive and a negative level, the integrand in equation (31.5) will remain unchanged on inversion, and so it may differ from zero. Transitions between a positive and a negative rotational level are thus permitted.

By the use of arguments exactly analogous to those in the preceding paragraph, it can be shown that the selection rule, for g and u electronic states, is that combination between two g states or between two u states cannot occur. On the other hand, a transition between a g state and a u state is possible.

The selection rules just derived may be combined to yield a result of considerable importance. The only transitions permitted are between a positive rotational level in a g state and a negative level in a u state, on the one hand, or between a positive level in a u state with a negative level in a g state, on the other hand. The possible transitions are therefore, as follows:

$$\bar{g}^+ \leftrightarrow \bar{u}^- \quad \text{and} \quad \bar{g}^- \leftrightarrow \bar{u}^+.$$

It was seen in Section 31c that both \bar{g}^+ and \bar{u}^- correspond to rotational levels that are symmetric in the nuclei, whereas \bar{g}^- and \bar{u}^+ refer to levels that are antisymmetric. It follows, therefore, that transitions are permitted between two symmetric rotational levels or between two antisymmetric rotational levels, but not between a symmetric and an antisymmetric level.

If a given homonuclear molecular species is initially all in one state, with either symmetric or antisymmetric rotational levels, then it will always remain in that state. Alternate rotational levels only will thus be occupied, and as a consequence alternate rotational lines will be missing from the

spectrum. It will be seen shortly that under normal conditions the molecules will all be either symmetric or antisymmetric exclusively, only if the nuclei have no spin momentum. This is the case, for example, with such homonuclear molecules as $^4\text{He}_2$, $^{16}\text{O}_2$, $^{12}\text{C}_2$ and $^{32}\text{S}_2$, and in the spectra of these substances alternate rotational lines are, in fact, missing. When the nuclear symmetry is destroyed by an isotopic exchange, as in the molecule of $^{16}\text{O}^{18}\text{O}$, the question of symmetric and antisymmetric levels does not arise, and all the rotational levels appear. It will be recalled that in Section 30d mention was made of the fact that the A band of oxygen, due to $^{16}\text{O}^{16}\text{O}$, has half as many rotational lines as the corresponding A' band for $^{16}\text{O}^{18}\text{O}$.

31e. Effect of Nuclear Spin: Ortho and Para States.²—The nuclei of many atoms possess a resultant intrinsic angular momentum, generally referred to as *nuclear spin*; the corresponding spin quantum number i gives the number of units of spin momentum of the nucleus. The spin vectors of two nuclei forming a diatomic molecule combine to yield a resultant spin quantum number t . When i is $\frac{1}{2}$, as for the hydrogen nucleus, there are two possible values for t , namely *unity*, for parallel nuclear spins, and *zero*, for antiparallel spins. It appears that each type of resultant spin is associated with either symmetric or antisymmetric rotational states, and no transitions are possible between them.

Each resultant molecular spin is $2t + 1$ -fold degenerate, because there are this number of possible orientations in a magnetic field, corresponding to the components $t, t - 1, t - 2, \dots, 0, \dots, -(t - 1), -t$ (cf. Section 2b). Hence, when t is 1 there are three possible orientations, whereas when t is zero, the number of orientations is unity. The probability or "statistical weight" of the molecular state with parallel spins ($t = 1$) is thus three times as great as that for the state with antiparallel spins ($t = 0$). It follows, therefore, that the probability of the occurrence of one set of rotational states, either symmetric or antisymmetric, will be three times as great as for the other. It was seen in the preceding section that transitions are possible between two symmetric states or between two antisymmetric states, and since one of these is three times as common as the other, the intensities of alternate rotational lines in the spectrum will be in the ratio of three to one.

Such an alternation of intensities of three to one has been observed in the spectrum of ordinary molecular hydrogen, H_2 . In its ground state, this molecule has a $^1\Sigma_g^+$ term, and so the rotational levels with even values of J should be symmetric, while those with odd values of J should be antisymmetric (cf. Table XI). The strongest lines in the spectrum are found to be those having odd J values in the ground state; hence the antisymmetric rotational levels are associated with that form of molecular hydrogen in which the two nuclei have parallel spins, i.e., $t = 1$. For convenience of nomenclature, the molecules whose rotational levels are present in excess at equilibrium are said to be in *ortho states*, and those present in smaller amount are in *para states*. Thus, ordinary molecular hydrogen consists, at ordinary

² Farkas, "Orthohydrogen, Parahydrogen and Heavy Hydrogen."

temperatures, of three parts of orthohydrogen and one part of parahydrogen; in the para state the molecules occupy only the even rotational levels, while in the ortho state the odd levels only are occupied. If there were no interaction between the nuclear spins and the remainder of the molecule, transitions between symmetric and antisymmetric levels would be completely forbidden. In other words, it would be impossible to reverse the spin of one of the nuclei so as to convert an ortho molecule into one in the para state, or vice versa. However, there is generally a small interaction between the magnetic moment associated with nuclear spin and the rest of the molecule, so that there is a small probability of transition between symmetric and antisymmetric levels. The rate of reversal of spin is so small, however, that in the absence of a catalyst, pure parahydrogen can be kept for a considerable time without conversion into the ortho form, although the system at equilibrium should consist of one part of the former to three of the latter. For reasons which will be made clear in Section 63b, the ratio of three parts of the ortho state to one part of the para state in ordinary hydrogen is the equilibrium ratio which is attained only when the temperature is sufficiently high, about 273° K in this case.

The existence of ortho and para states in different proportions, corresponding to symmetric and antisymmetric states, should be of general occurrence for all homonuclear diatomic molecules, and even for symmetrical linear polyatomic molecules, such as acetylene, some of whose nuclei possess spin quantum numbers which differ from zero. If the spin of each nucleus is i , the resultant spin of the diatomic molecule can then be $2i, 2i - 1, 2i - 2, \dots, 2, 1, 0$. Of these, the first, third, fifth, etc., have been proved to correspond to one set of rotational (antisymmetric) levels, while the second, fourth, sixth, etc., refer to the other set of (symmetric) levels. In general, therefore, the resultant nuclear spin may be written as $2i - n$, where n is an integer which cannot exceed $2i$, so that $2i - n$ is always positive. For the ortho states, i.e., those present in excess at equilibrium, n must be even, including zero, and for the para states n is odd. As seen above, each resultant molecular spin is $2i + 1$ -fold degenerate, and so the multiplicity of any state is given by the general expression $2(2i - n) + 1$. Since n is even for the ortho states and odd for the para states, it follows that

$$\frac{\text{Statistical Weight of Ortho States}}{\text{Statistical Weight of Para States}} = \frac{\sum_{n=0, 2, 4, \dots} 2(2i - n) + 1}{\sum_{n=1, 3, 5, \dots} 2(2i - n) + 1} \quad (31.6)$$

$$= \frac{(i + 1)(2i + 1)}{i(2i + 1)}. \quad (31.7)$$

The ratio of the statistical weights or probabilities, which is seen to be equal to $(i + 1)/i$, gives the limiting proportion of ortho form to para form at equilibrium.

It should be noted that equation (31.7) also represents the ratio of the intensities of alternate rotational lines in the band spectrum under equi-

librium conditions at appreciable temperatures. When the nuclear spin i is zero the ratio of the intensities of alternate rotational lines is equal to 1/0; in other words, alternate lines, with zero intensity, should be missing. This result is in agreement with the conclusion reached earlier when nuclear spin was not taken into consideration. The reverse of the argument is also true; when alternate lines are missing, as in the electronic spectrum of the $^{16}\text{O}^{16}\text{O}$ molecule, the spin of each ^{16}O nucleus is zero.

There is one further matter that must be mentioned, although it will not be possible to go into details. It has been seen that the ratio of ortho states to para states is given by $(i + 1)/i$, but nothing has been said concerning the question as to which states correspond to symmetric and which to anti-symmetric rotational levels. The actual distribution depends on various symmetry considerations, and also on whether the nuclei obey the Bose-Einstein or the Fermi-Dirac statistics (of. Chapter VII). If the Fermi-Dirac statistics are followed, as appears to be the case for all nuclei of odd mass number, the antisymmetric levels are ortho, and the symmetric levels are para. On the other hand, for nuclei of even mass number, the Bose-Einstein statistics are obeyed, and the symmetric levels are ortho, while the anti-symmetric are para. With hydrogen, for example, the atomic mass number is odd, and so Fermi-Dirac statistics are applicable. The antisymmetric levels then constitute the ortho state, present in excess at equilibrium. Reference to Section 31c shows that these are the levels with odd J values, since normal hydrogen is in a $^1\Sigma_g^+$ state. The heavier isotope of hydrogen, namely deuterium, with even mass number, follows the Bose-Einstein statistics, and so the symmetric levels should be present in larger proportion. Since molecular deuterium is also in a $^1\Sigma_g^+$ state, the rotational levels with even J values constitute the ortho state. Further reference to the properties of ortho and para states will be made in Chapter VIII.

31f. Selection Rules for Electronic Transitions.—The nature of the electronic transitions that are permitted depend to some extent on the type of coupling between electronic and rotational energies; the selection rules given here apply particularly to molecules exhibiting case (a) or case (b) coupling. The quantum number Λ can change only by zero or ± 1 , so that transitions such as

$$\Sigma \leftrightarrow \Sigma, \Pi \leftrightarrow \Pi, \Delta \leftrightarrow \Delta, \Sigma \leftrightarrow \Pi \text{ and } \Pi \leftrightarrow \Delta$$

are possible, but $\Sigma - \Delta$, $\Sigma - \Phi$, etc., are not observed. Another rule is that the resultant spin is usually unchanged in an electronic transition, so that combination occurs between states of equal multiplicity; thus, $^1\Sigma \leftrightarrow ^1\Sigma$, $^2\Pi \leftrightarrow ^2\Delta$, and so on. Further, positive electronic states combine only with positive states, and negative with negative, so that there are no transitions of the type $\Sigma^+ - \Sigma^-$.³ If one of the combining levels is a Σ state and the other is not, then it is immaterial whether the former is positive or negative, so that the transitions $\Sigma^+ \leftrightarrow \Pi$ and $\Sigma^- \leftrightarrow \Pi$ can both occur. Finally, as

³ This rule should not be confused with that given in Section 31d, according to which transitions occur only between positive and negative *rotational levels*.

stated in Section 31d, for diatomic molecules with equally, or almost equally, charged nuclei, transitions can occur only between a g state and a u state; transitions between two g states or between two u states are not permitted.

APPLICATIONS OF POTENTIAL ENERGY CURVES

32a. Potential Energy Curves.—If the oscillations of the nuclei in a diatomic molecule were simple harmonic in character, the potential curve, representing the variation of potential energy with internuclear distance, would be a simple parabola, as shown by the dashed curve in Fig. 22. Because of the known anharmonic nature of the nuclear vibrations, the actual potential energy curve for a diatomic molecule will be of the form indicated by the full line in the figure (cf. Fig. 9). The minimum of the curve will be taken here as the arbitrary energy zero, so that the vibrational energy, given by the equation

$$E_v = (v + \frac{1}{2})hc\omega_e - (v + \frac{1}{2})^2hc x\omega_e + \dots \quad (32.1)$$

will be referred to this zero. The vibrational energy levels, for various values of the quantum number v , namely 0, 1, 2, 3, \dots , derived from this equation, are indicated by the horizontal lines. The energy difference between the bottom of the curve and the $v = 0$ vibrational level is equal to the zero-point energy E_0 , defined by

$$E_0 = \frac{1}{2}hc\omega_e - \frac{1}{4}hc x\omega_e + \frac{1}{8}hc y\omega_e + \dots \quad (32.2)$$

In any vibrational state, such as that represented by the line LN , for example, the variation of potential energy as the nuclei approach and recede is represented by the curve NML . As the potential energy diminishes, the kinetic energy of vibration increases correspondingly, so that the total energy remains constant, equal to E_v for the level LN .

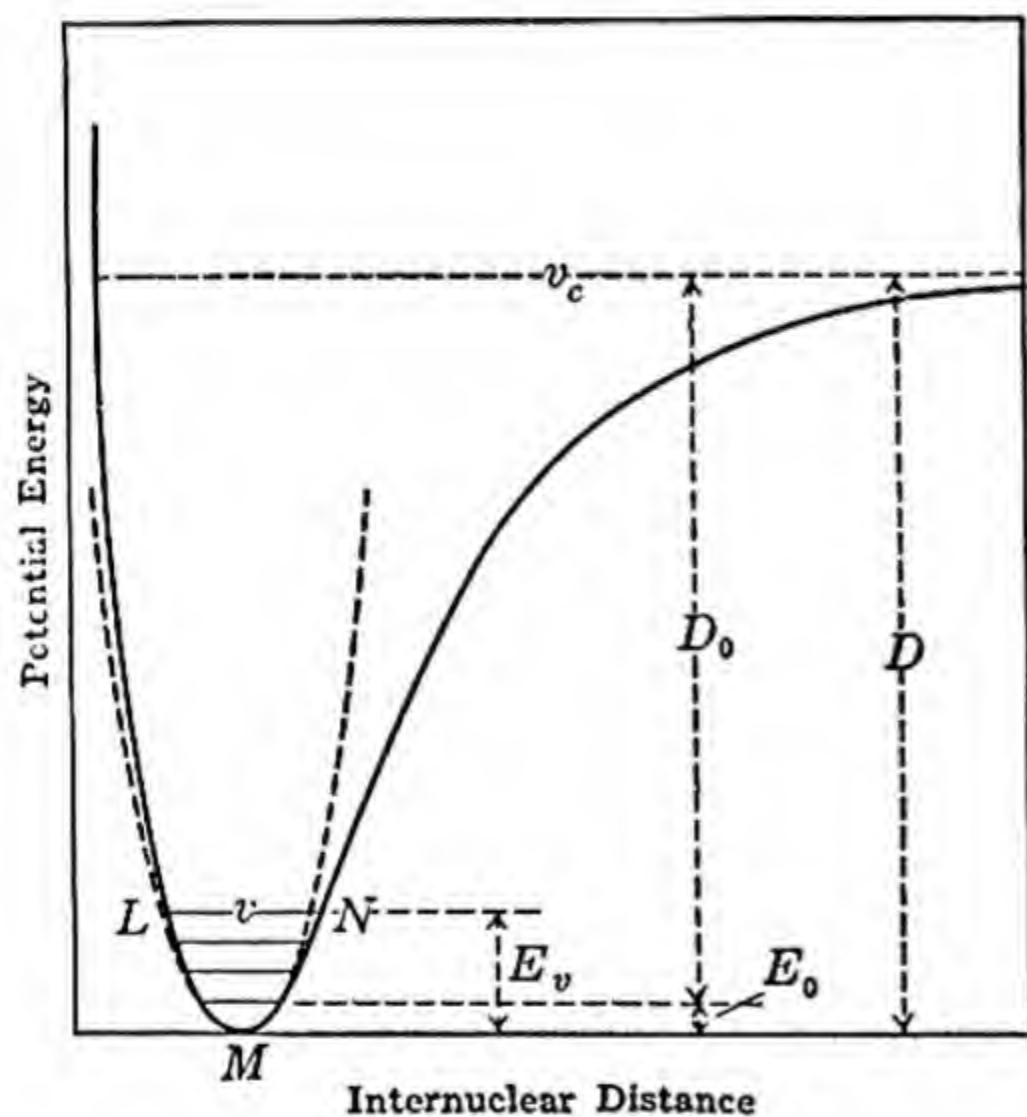


FIG. 22. Potential energy curve

It will be evident from the shape of the full curve compared with that of the dashed curve, that provided the vibrational quantum number is small, the oscillations are approximately simple harmonic. For higher vibrational levels, however, considerable deviations due to anharmonicity occur, and the result is that when the vibrational energy is high enough, viz., at v_c in Fig. 22, the distance between the nuclei becomes infinite in the course of an

oscillation. That is to say, it should be possible to cause a molecule to dissociate into its constituent atoms by supplying it with sufficient vibrational energy. This type of dissociation does not commonly occur in the ground state of the molecule, but it will be seen in Section 32d that as a result of an electronic transition the vibrational energy of the molecule in the final state is sometimes sufficient to permit the nuclei to recede to infinite separation. The potential energy of the molecule corresponding to the level v_c , which is the lowest at which dissociation into atoms can occur, is equal to the heat of dissociation (cf. Section 32e). Two values of this heat are defined, as shown in Fig. 22; the value reckoned from the lowest actual vibrational ($v = 0$) level, is given the symbol D_0 ; this is really equal to the (hypothetical) heat of dissociation at 0°K . On the other hand, the heat of dissociation referred to the bottom of the potential energy curve, which is equal to the maximum vibrational energy, will be represented by D , so that

$$D = D_0 + E_0, \quad (32.3)$$

where E_0 is the zero-point energy.

32b. The Morse Equation.⁴—The potential function $U(r)$ for a diatomic molecule undergoing simple harmonic oscillations, may be written as

$$U(r) = f(r - r_e)^2, \quad (32.4)$$

where r is the actual distance between the nuclei and r_e is the equilibrium value; the latter is the internuclear distance at the minimum of the potential energy curve; f is a constant, actually equal to twice the force constant. In order to allow for anharmonicity, it would be necessary to add further terms (cf. Section 29b), so that

$$U(r) = f(r - r_e)^2 + g(r - r_e)^3 + h(r - r_e)^4 + \dots \quad (32.5)$$

Such an expression can possibly be represented as an exponential function of $r - r_e$, and Morse proposed the relationship

$$U(r) = D\{1 - e^{-a(r-r_e)}\}^2, \quad (32.6)$$

where D is the heat of dissociation defined above, and a is a constant for the given molecule. The Morse function satisfies most of the requirements of an actual potential curve. If r is put equal to r_e , the value of $U(r)$ is seen to be zero, whereas as r approaches infinity, $U(r)$ becomes equal to D , the heat of dissociation; these results are in agreement with actual fact. However, as r approaches zero, the value of $U(r)$ should approach infinity, although the Morse function leads to a finite result. This discrepancy is not serious; first, because the potential energy given by the Morse function is, in any case, very large when r is zero, and second, because the conditions for internuclear distances that approach zero are of no practical significance.

⁴ Morse, *Phys. Rev.*, **34**, 57 (1929); see also, Hulburt and Hirschfelder, *J. Chem. Phys.*, **9**, 61 (1942).

If the Morse function is used to represent the potential energy of an oscillator, the Schrödinger equation leads to the result

$$E_v = a \sqrt{\frac{D}{2\pi^2 c^2 \mu}} (v + \frac{1}{2})hc - \frac{ha^2}{8\pi^2 c \mu} (v + \frac{1}{2})^2 hc \quad (32.7)$$

for the eigenvalues of the total energy of the oscillator; this expression is obviously of the form [cf. equation (32.1)]

$$E_v = (v + \frac{1}{2})hc\omega_e - (v + \frac{1}{2})^2 hc x \omega_e, \quad (32.8)$$

and so it follows that the constant a in equation (32.6) is given by

$$a = \omega_e \sqrt{\frac{2\pi^2 c^2 \mu}{D}}, \quad (32.9)$$

where μ is the reduced mass of the molecule. Further, it follows from a comparison of the coefficients of $(v + \frac{1}{2})^2$ in equations (32.7) and (32.8) that

$$x\omega_e = \frac{ha^2}{8\pi^2 c \mu}, \quad (32.10)$$

giving as an alternative definition of a ,

$$a^2 = \frac{8\pi^2 c x \omega_e \mu}{h}. \quad (32.11)$$

Finally, from equations (32.9) and (32.10), it is seen that

$$D = \frac{hc\omega_e}{4x}. \quad (32.12)$$

The values of a and D required for the Morse equation can thus be calculated if ω_e and x are known. Although several other potential functions have been proposed, the Morse equation is the most widely used, partly because of its satisfactory agreement with experiment, and partly on account of its simplicity.

32c. Electronic Transitions: The Franck-Condon Principle.—Every electronic state of a molecule has its own potential energy curve; the forms of these curves are usually completely unrelated, although certain general considerations regarding their nature will be developed in later sections. Two curves, for a lower electronic state A and an upper electronic state B are shown in Fig. 23; the nuclear separations at equilibrium, i.e., at the minima of the curves, are different in the two cases, and so also are the heats of dissociation. The vertical distance between the minima of the curves is equal to the difference in the electronic energy of the two states; this is the quantity represented by the symbol E_e , and is equivalent to $h\nu_e$ in Section 30a

The probability of the transition from a given vibrational level in the lower state to any level in the upper state, when radiation is absorbed, or of the reverse process when radiation is emitted, is determined by a rule, first stated by Franck⁵ and later developed quantum mechanically by Condon.⁶ The rule is consequently known as the *Franck-Condon principle*. According to this principle, transitions from one state to another are most probable when the nuclei are in their extreme positions, e.g., at L and N for the level LN in Fig. 22, for it is there, when the vibrational kinetic energy is zero, that they spend the longest time. In other words, it is near the extreme positions of the nuclei where the square of the vibrational eigenfunction is greatest. Further, since the time required for an electronic transition is very small compared with the time necessary for the nuclei to oscillate, the internuclear distance will remain virtually constant during the course of an electronic change. This means that electronic transitions will be represented by vertical lines, and the most probable transitions will be those commencing from the extreme positions of the nuclei for any given vibrational level; one transition of this kind is shown in Fig. 23.⁷ Since these are the most probable, the corresponding vibrational bands in the electronic spectrum will be the most intense. The particular vibrational transitions producing these bands will, of course, depend on the relationship between the upper and lower potential energy curves. It is easy to understand, therefore, why it is not possible to state a simple selection rule for vibrational changes accompanying electronic transitions.

As already mentioned in Section 29b, the absorption bands starting from the $v = 0$ level in the ground state must always be the most intense, at least at ordinary or low temperatures. In emission, however, the molecules in the excited state will occupy several of the vibrational levels, and a variety

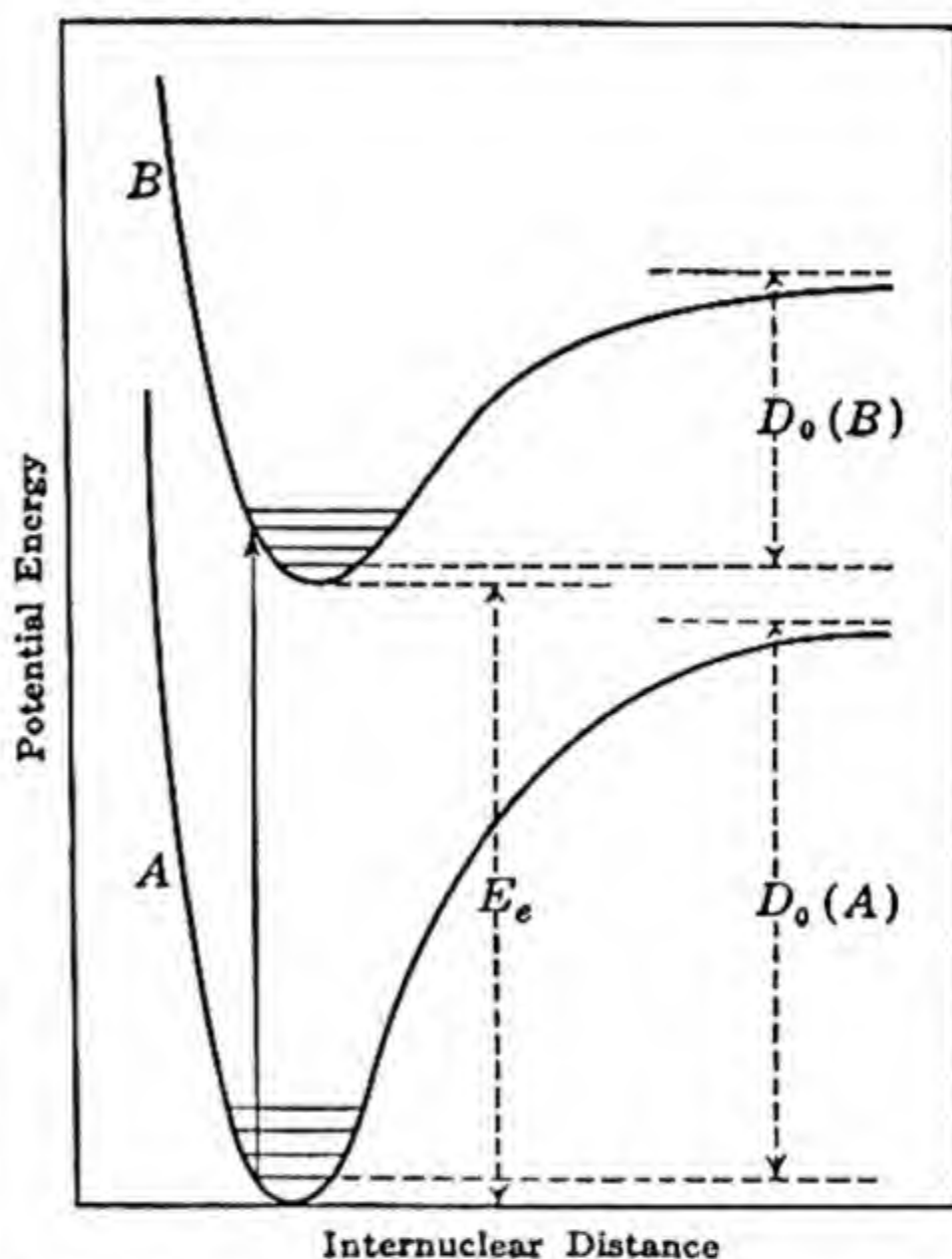


FIG. 23. Potential energy curves of lower (A) and upper (B) electronic states

⁵ Franck, *Trans. Faraday Soc.*, 21, 536 (1926); *Z. phys. Chem.*, 120, 144 (1926).

⁶ Condon, *Phys. Rev.*, 28, 1182 (1926); 32, 858 (1928).

⁷ The quantum mechanical treatment indicates that for the lowest ($v = 0$) vibrational level, the square of the eigenfunction has a single maximum at a position corresponding to the midpoint of the classical vibration. The electronic transition from this level should thus take place from a central point rather than from the extreme positions of the nuclei (cf. Pauling and Wilson, "Introduction to Quantum Mechanics," page 74).

of transitions to the ground state, all governed by the Franck-Condon principle, will be possible. The relative intensities of the bands corresponding to various vibrational transitions have been satisfactorily explained in this manner. It should be remembered that the transitions represented by vertical lines on the potential energy diagram and starting from the extreme positions of the nuclei will be the most probable, but other transitions will also occur; since the latter are less probable, however, the corresponding bands will be less intense.

32d. Dissociation in Electronic Transitions.—In the electronic transition depicted in Fig. 23, the molecule has a definite amount of vibrational energy in both upper and lower states; the spectrum corresponding to such

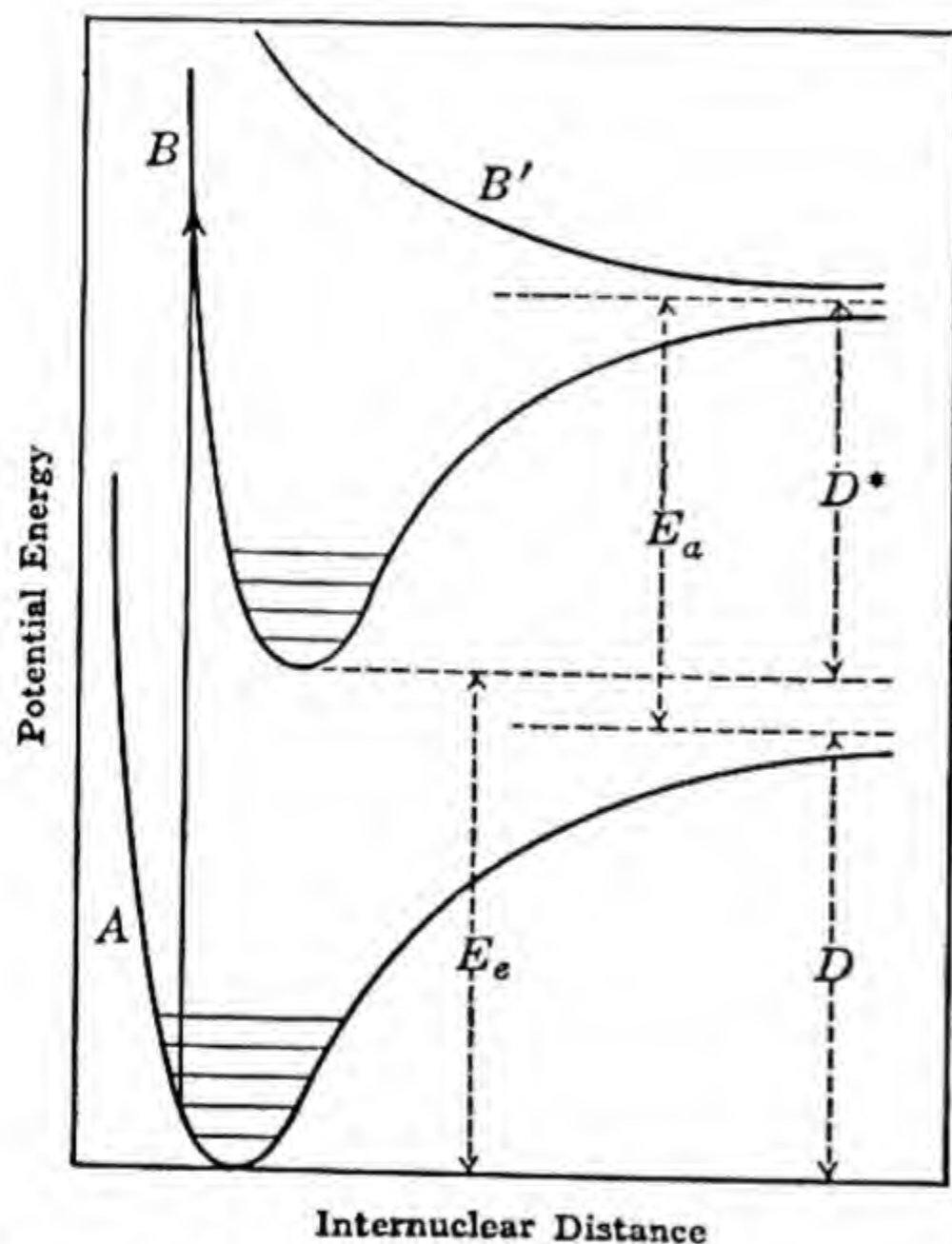


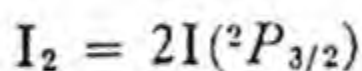
FIG. 24. Dissociation in an electronic transition

transitions exhibits definite vibrational bands. If the potential energy curves of the two electronic states are related somewhat in the manner depicted in Fig. 24, however, certain transitions, such as the one shown, will be accompanied by dissociation. The vibrational energy in the upper state is so high that the internuclear distance becomes infinite in the course of a vibration. When this type of transition is possible, the electronic absorption spectrum may consist of a number of bands, corresponding to transitions from the ground state to definite vibrational levels in the upper state, but these bands will converge and eventually pass into a continuous region showing no band structure. In this continuous region, or *continuum*, there is no complete vibration of the molecule, because the vibrational energy in

the upper state is sufficient to bring about dissociation. Absorption spectra of this type, in which a series of vibrational bands, complete with rotational fine structure, converge and eventually become a continuum, have been observed with iodine and other halogen molecules, and also in certain electronic spectra of molecular hydrogen and oxygen.

If the absorption spectrum is obtained at ordinary temperatures, then the energy corresponding to the convergence limit frequency is the minimum amount which must be supplied to the lowest vibrational level ($v = 0$) in the ground state in order to bring about dissociation in the upper electronic state. For example, by means of a short extrapolation of the rapidly converging vibrational bands in the absorption spectrum of molecular iodine,

the *convergence limit*, where the continuous spectrum commences, is found to occur at a wave length of 4995 Å. The corresponding energy, according to the quantum theory, is 57,200 cal. per mole. Hence this amount of energy must be supplied to a mole of gaseous iodine in the ground state before it will dissociate into iodine atoms. Attention must be called at this point to the fact that the products are not necessarily iodine atoms in their ground states. The question of the nature of the products of dissociation will be treated later (Chapter VI), but in the meantime it may be stated that there are many good reasons for believing that dissociation of an iodine molecule in the upper electronic state leads to the formation of at least one excited atom. The excitation energy of this atom is represented by E_a in Fig. 24, on the assumption that dissociation in the ground state of the molecule leads to two normal atoms. When dissociation of iodine occurs at 4995 Å, the products are probably one normal ($^2P_{3/2}$) and one excited ($^2P_{1/2}$) iodine atom. From the spectrum of atomic iodine the energy difference (E_a) of these two states is known to be 21,720 cal. per g. atom, and so it follows that D_0 for the reaction



is 57,200 – 21,720, i.e., 35,480 cal. per mole. This result has been verified by observations on the convergence limit of a weak band system of molecular iodine in the red portion of the spectrum; the products of dissociation are then two normal ($^2P_{3/2}$) iodine atoms. The agreement of the heat of dissociation with that just calculated is very satisfactory.

By determining the position of the convergence limit, where the discrete band spectrum passes over into a continuum, it is consequently possible to ascertain the heat of dissociation of molecular iodine. Determinations similar to those described above, have been made of the D_0 values of chlorine, bromine, hydrogen and oxygen. The products are usually a normal and an excited atom, and the accuracy of the result depends not only on a precise knowledge of the convergence limit, but the energy of excitation of the atom must also be known accurately. Nevertheless, it is possible to determine the heats of dissociation of such molecules as hydrogen and oxygen with an accuracy that is greater than by direct thermochemical methods.

In some cases the electronic absorption spectrum shows no banded structure, but is continuous throughout. This occurs when the potential energy curve in the upper electronic state is of the type shown in Fig. 24 at B' ; that is to say, the potential curve has no minimum. In this event, every possible transition from lower to upper state is accompanied by dissociation, and consequently there can be no vibrational structure. The molecule in the upper electronic state is incapable of performing a complete oscillation, for it must undergo dissociation in the process. In the state represented by B' the molecule is unstable (cf. Fig. 9), but electronic states of this type are frequently involved in electronic transitions. Completely continuous spectra, with no vibrational bands, are also observed in emission when the upper

state has a potential energy curve with a minimum, but the lower state is unstable. This would be similar to the $A \rightarrow B'$ transition with the positions of the curves reversed.

32e. Calculation of Heat of Dissociation.—For many molecules the vibrational bands cannot be followed, generally because of their faintness, right up to the convergence limit; in such cases an approximate estimate of the heat of dissociation can be made by using an analytical extrapolation procedure.⁸ If a diatomic molecule were a truly harmonic oscillator, the energy (or frequency) separation of successive bands would be constant, and no convergence limit, or dissociation, would occur (cf. dashed curve in Fig. 22). For an anharmonic oscillator, however, the energy (or frequency) separations of the origins of successive bands in a given progression steadily diminish, and eventually become zero at the convergence point. It may be seen from equation (32.1) that the energy difference ΔE_v between the origins of two adjacent vibrational bands is given by

$$\Delta E_v = hc\omega_e - 2(v + \frac{1}{2})hc x \omega_e. \quad (32.13)$$

It is evident from this expression that ΔE_v will decrease regularly as v increases, and the condition that ΔE_v shall be zero gives the vibrational quantum number v_c at the dissociation (convergence) limit; thus

$$\begin{aligned} hc\omega_e - 2(v_c + \frac{1}{2})hc x \omega_e &= 0, \\ v_c &= \frac{1 - x}{2x}. \end{aligned} \quad (32.14)$$

If this is substituted in equation (32.1), the vibrational energy at the convergence limit, which is equal to the heat of dissociation D for the given state (cf. Fig. 22) is then seen to be

$$D = \frac{hc\omega_e}{4x}. \quad (32.15)$$

[It is of interest to note that this result is identical with equation (32.12) derived from the treatment of the Morse equation.] The value of D_0 , which is the ordinary heat of dissociation for 0°K. , with all the molecules assumed to be in the lowest vibrational ($v = 0$) and rotational ($J = 0$) levels, is then obtained from D by subtracting the zero-point energy [cf. equation (32.3)]; thus, taking the latter as $\frac{1}{2}hc\omega_e$ [cf. equation (32.2)],

$$\begin{aligned} D_0 &= D - E_0 \\ &= \frac{hc\omega_e}{4x} - \frac{hc\omega_e}{2}. \end{aligned} \quad (32.16)$$

Insertion of the known values of ω_e and x will give the heat of dissociation D_0 per single molecule; multiplication by the Avogadro number then yields

⁸ Birge and Sponer, *Phys. Rev.*, 28, 259 (1926).

the value per mole. If ω_e and x are the values for the ground state of the molecule, then D_0 will refer, of course, to the products of this state, which may, or may not, be the normal atoms. If one or both of the atoms is in an electronically excited state, the necessary allowance for the excitation energy must be made in calculating the heat of dissociation with normal atoms as products.

From a study of the electronic spectra of molecular hydrogen, it has been found that in the ground state, ω_e is 4405.3 cm.^{-1} and $x\omega_e$ is 125.32 cm.^{-1} ; hence x is 0.028447, and

$$D_0 = 6.624 \times 10^{-27} \times 3 \times 10^{10} \times 4405 \left(\frac{1}{0.1138} - 0.5 \right) \text{ ergs per molecule} \\ = 104.4 \text{ kcal. per mole.}$$

This result may be compared with the value of 102,680 cal. obtained by Beutler (1934), by accurate graphical extrapolation over a short range. The products of dissociation are evidently two normal atoms in this case.

Another possibility is to use ω_e and x in equation (32.16) as determined for a higher electronic state of the molecule; the quantity given by equation (32.16) is then equal to D_0^* , the heat of dissociation in this electronic state. In order to determine D_0 in the ground state it is necessary to make allowance for the electronic energy E_e and the excitation energy E_a of the products. It is seen from Fig. 24 that

$$D = D^* + E_e - E_a,$$

where D^* refers to the upper state. Since D_0 is equal to $D - E_0$, as seen above, and D_0^* is equal to $D^* - E_0^*$, and neglecting the difference between E_0 and E_0^* , it follows, as a first approximation, that

$$D_0 = D_0^* + E_e - E_a. \quad (32.17)$$

As seen previously, E_e is equal to $h\nu_e$, and ν_e may be determined from spectroscopic data, as shown in Section 30a. The calculation may be illustrated by reference to the Schumann-Runge bands for oxygen, which give the following values: $\nu_e = 49,052 \text{ cm.}^{-1}$, $\omega_e = 710.14 \text{ cm.}^{-1}$ and $x\omega_e = 11.705$. These data give 169,000 cal. per mole for the sum of D_0^* and E_e . The products of dissociation are probably one normal (3P) atom and one excited (1D) atom, the excitation energy of the latter being 1.97 e.v., or 45,400 cal. If this is taken as the value of E_a , it is found that D_0 is about 123,000 cal., which may be compared with the value obtained from an accurate estimate of the convergence limit, viz., 117,200 cal., per mole.

An important source of error⁹ in the use of equation (32.16) for calculating heats of dissociation lies in the fact that the determination of ν_e by equation (32.14) is based on (32.13), according to which ΔE_v should be a linear function of the vibrational quantum number v . An examination of actual

⁹ Birge, *Trans. Faraday Soc.*, 25, 707 (1929).

spectra shows that ΔE_v is in many cases a linear function of v for small values of the latter, but for higher vibrational quantum numbers successive values of ΔE_v decrease more rapidly than would be expected from equation (32.13). The reason for this discrepancy is the neglect of terms involving $(v + \frac{1}{2})^3$, $(v + \frac{1}{2})^4$, etc., in the complete expression for the energy of an anharmonic oscillator. If these were included, with appropriate values for the anharmonicity constants y , z , etc., ΔE_v would no longer be expected to vary in a linear manner with the vibrational quantum number. For small values of v the difference is negligible, but for high values, such as are concerned in the extrapolation, the errors introduced by the neglect of the higher terms are significant. The true value of v_c , the vibrational quantum number at the convergence limit, is almost invariably less than that given by equation (32.14), and so the heats of dissociation from equation (32.16) are generally too high, as seen above. The calculation could be improved by introducing the higher powers of $v + \frac{1}{2}$, but this would require a knowledge of the anharmonicity constants. A better procedure is to plot the experimental results for ΔE_v , derived from the band spectrum, against v , from $v = 0$ to the highest available value, and then to extrapolate the resulting curve graphically until it cuts the v axis. At this point ΔE_v is zero, and the corresponding value of v is equal to v_c . The area enclosed by the curve and the two axes is then the sum of all the ΔE_v terms from $v = 0$ to $v = v_c$; this is clearly equal to D_0 , the heat of dissociation in the given electronic state.

32f. Predissociation.—In certain cases an electronic spectrum has been observed in which there are a number of vibrational bands with the expected fine (rotational) structure; from a certain band onwards, however, the rotational lines are replaced by a diffuse structure. These diffuse bands are referred to as *predissociation spectra*.¹⁰ The fact that the band structure is still evident suggests that the molecule has definite vibrational energy levels in upper and lower electronic states, but for some reason the rotational energy is not quantized. In some cases the predissociation spectrum is followed by a region of continuous absorption but, in other instances, bands with fine structure are found on both long and short wave sides of the predissociation bands.

It is probable that there are several types of predissociation, but in general the production of the diffuse spectra can be accounted for by supposing that the molecule is first raised from one electronic level to another, and at the same time there are a number of vibrational transitions. The vibrational bands thus appear clearly in the electronic band system. If the energy acquired by a molecule in this transition is greater than is necessary in another excited electronic state, this energy may redistribute itself so as to cause the molecule to dissociate. If the time elapsing between acquisition of the necessary energy and its redistribution is small compared with a period of rotation, the molecule will dissociate before a complete rotation can occur.

¹⁰ Henri, *Compt. rend.*, 179, 1156 (1924); *Trans. Faraday Soc.*, 25, 765 (1929); Herzberg, *Z. Physik*, 61, 604 (1930).

The rotation will thus not be quantized, i.e., definite rotational levels will be absent, and the vibrational band will not show fine structure.

The situation may be considered more precisely by means of potential energy curves. It is probable that in many, if not all, cases of predissociation, three different electronic energy levels are concerned; in addition to the curves *A* and *B*, representing the lower and upper electronic states taking part in the primary transition, there is a third state *C*, whose potential energy curve crosses *B* (Fig. 25).

Normally, direct transitions from *A* to *C* do not occur, but a *radiationless transition*, involving no energy change, from *B* to *C* is possible, provided the potential energy is in the vicinity of the point *P* where the curves *B* and *C* cross. As a result of the transition $A \rightarrow B$, represented by the line I, the molecule in state *B* will vibrate normally, and a vibration band with fine structure will appear. For a transition such as II, however, as the nuclei recede in state *B*, the energy passes through the point *P* and a transition to *C* can take place. The energy of the system, although not great enough to dissociate the state *B*, is now greater than is required to bring about dissociation of *C*, and so this occurs. The vibration in state *B* is still quantized, but for transitions like II, and beyond, the molecule dissociates, after passing into state *C*, in less time than a period of rotation, and so the rotational fine structure ceases. If the transition from *A* to *B* is one which leads to a relatively high energy in state *B*, then the vibrational kinetic energy of the molecule as it passes through the point *P* may be so large that the transition to state *C* does not occur. In this case, the predissociation region will be followed by bands showing discrete rotational structure.

The radiationless transition from one state in which the energy is quantized to another in which it is not, is frequently referred to as the *Auger effect*. It was first observed with X-rays, and it was later shown to occur in connection with atomic spectra. In general, when a series of quantized levels, in one particular state of an atom or molecule, overlap the continuum of another state, a radiationless transition, i.e., without change in electronic, vibrational or rotational energy, is possible from one state to the other, provided the selection rules concerning an electronic transition are not

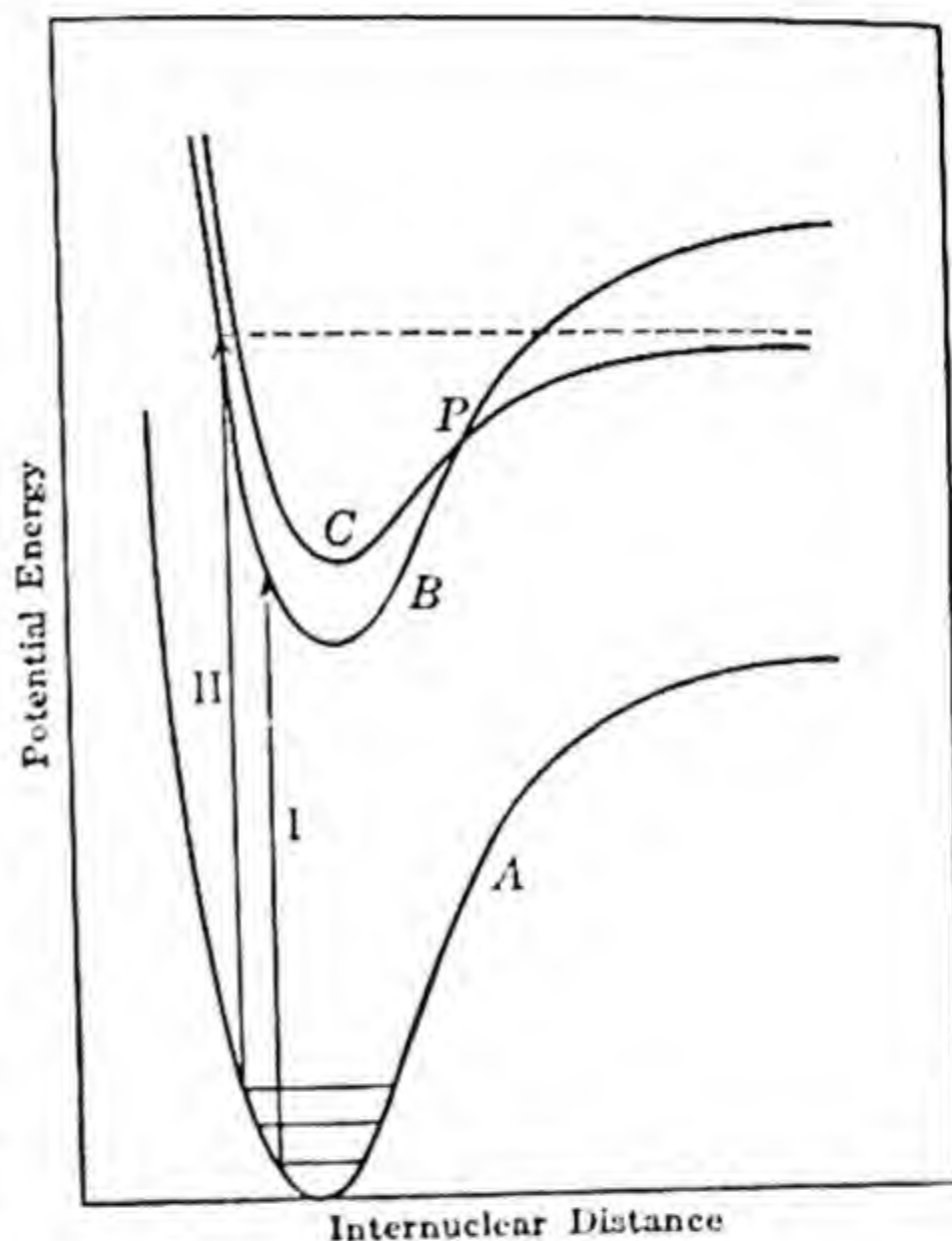


FIG. 25. Potential energy curves for predissociation

violated. This overlap occurs with the states B and C in Fig. 25, since the dissociation limit of C lies below that of B ; when the two curves cross at the point P , the radiationless transition can occur in accordance with the Franck-Condon principle.

A consideration of the curves in Fig. 25 shows that the energy corresponding to the frequency of the predissociation limit, that is, the point at which the vibrational bands become diffuse, is equal to the energy that must be supplied to the lower state A in order to bring about dissociation in the state C . Actually, because of the shapes of the curves, it is probably safer to say that the predissociation limit gives a maximum for this dissociation energy. The approximate values of the heats of dissociation of a number of compounds have thus been calculated from predissociation spectra. Apart from its quantitative aspects, the occurrence of predissociation in certain spectral regions is important in the investigation of photochemical reactions, for it shows that the absorption of radiation in these regions is accompanied by dissociation of the molecule.

THE RAMAN EFFECT¹¹

33a. Scattering of Light.—In the normal scattering of light by a solid, liquid or gas, the frequency of the radiation is unchanged; that is to say, the incident light and the scattered light have the same frequency. Scattering of this type is known as *Rayleigh scattering*. Further examination of scattered light has shown that in addition to Rayleigh scattering, there exists, to a very much smaller extent, a form of scattering in which the frequency of the light undergoes a definite change. This new form of scattering, predicted theoretically by Smekal in 1923, and observed and studied in 1928 by Raman, is called *Raman scattering*. The Raman effect has been observed with all forms of matter, and its essential nature is independent of the frequency of the incident light. The scattered Raman radiation contains frequencies that are both larger and smaller than that of the incident light, assuming the latter to be monochromatic. The differences, however, are characteristic of the substance producing the scattering, and do not depend on the frequency of the light employed. If ν_i is the frequency of the incident radiation, and ν_s is that of the light scattered by a given molecular species, then the *Raman shift* $\Delta\nu$, defined by

$$\Delta\nu = \nu_i - \nu_s, \quad (33.1)$$

is characteristic of the particular species. When $\Delta\nu$ is positive, that is, when the frequency of the scattered radiation is less than that of the incident light, the Raman spectrum is said to consist of *Stokes lines*; if, however, ν_s is greater than ν_i , so that $\Delta\nu$ is negative, the Raman lines are referred to as

¹¹ Bhagavantam, "Scattering of Light and The Raman Effect"; Glockler, *Rev. Mod. Phys.*, 15, 111 (1943); Hibben, "The Raman Effect and its Chemical Applications"; Kohlrausch, "Der Smekal-Raman Effekt" and the "Ergänzungsband, 1931-37."

anti-Stokes lines. For reasons which will be explained shortly, the Stokes lines are frequently much more intense than the anti-Stokes lines.

The Raman frequency shifts $\Delta\nu$ generally lie within the range of 100 cm.^{-1} to 3000 cm.^{-1} ; such frequencies correspond to radiations lying in the far and near infra-red regions of the spectrum, respectively. It appears probable, therefore, that the changes in energy of the scattered light in the Raman effect correspond to the energy changes accompanying rotational and vibrational transitions in a molecule. It will be seen below that there is, in fact, an almost exact correspondence between the Raman shifts and the observed or calculated vibrational and rotational frequencies.

33b. Classical Theory of the Raman Effect.—The simple classical theory of scattering may be employed to give an interpretation of the Raman effect. If an atom or molecule is placed in an electric field, the electrons and nuclei are displaced in such a manner as to induce a dipole moment in the atom or molecule. If F is the strength of the electric field and μ is the magnitude of the induced moment, then

$$\alpha = \mu F, \quad (33.2)$$

where α is the *polarizability* of the molecule. According to the electromagnetic theory of light, the variation with time t of the electric field, of strength F , accompanying radiation of frequency ν is given by the equation

$$F = F_0 \sin 2\pi\nu t, \quad (33.3)$$

where F_0 , a constant, is the equilibrium value of the field strength. Hence, by equation (33.2), the field F will induce a dipole moment which varies according to the expression

$$\mu = \alpha F_0 \sin 2\pi\nu t. \quad (33.4)$$

It follows, therefore, from this result that the light of frequency ν will induce in the atom or molecule with which it interacts, a dipole which oscillates with the same frequency ν . By classical theory, this oscillating dipole should emit, i.e., scatter, radiation of the identical frequency ν , and hence the result will be Rayleigh scattering, for which the incident and scattered radiations have the same frequency.

In this argument no account has been taken of the oscillation or rotation of the molecule, but the accompanying movements will affect the induced dipole moment, and hence they will influence the scattering. Suppose the molecule is assumed, as heretofore in the present chapter, to be diatomic; as the two nuclei vibrate along the line joining them the polarizability of the molecule will vary. For small displacements x from the equilibrium position, it is possible to represent the variation of polarizability α with the displacement by

$$\alpha = \alpha_0 + \beta \frac{x}{A}, \quad (33.5)$$

where α_0 is the equilibrium polarizability, β is the rate of variation of the

polarizability with displacement, and A is the vibration amplitude. If the oscillations of the molecule are simple harmonic, the variation of x with time may be represented by

$$x = A \sin 2\pi\nu_v t, \quad (33.6)$$

in which ν_v is the vibration frequency of the molecule for small displacements. It follows, therefore, from equations (33.5) and (33.6) that

$$\alpha = \alpha_0 + \beta \sin 2\pi\nu_v t, \quad (33.7)$$

and hence from equation (33.4), the variation of the induced dipole moment with time is given by

$$\begin{aligned} \mu &= \alpha_0 F_0 \sin 2\pi\nu t + \beta F_0 \sin 2\pi\nu t \sin 2\pi\nu_v t \\ &= \alpha_0 F_0 \sin 2\pi\nu t + \frac{1}{2}\beta F_0 \{\cos 2\pi(\nu - \nu_v)t - \cos 2\pi(\nu + \nu_v)t\}. \end{aligned} \quad (33.8)$$

According to this equation, the induced dipole moment oscillates not only with the frequency ν of the incident light, but also with the frequencies $\nu - \nu_v$ and $\nu + \nu_v$; these are smaller and larger, respectively, than that of the incident light by an amount equal to the vibration frequency ν_v of the diatomic molecule. The first of these frequencies of the oscillating dipole, i.e., ν , gives rise to scattered radiation of the same frequency as the incident light, that is, to Rayleigh scattering. In the other two frequencies, viz., $\nu - \nu_v$ and $\nu + \nu_v$, is to be found the origin of the Raman effect; the scattered radiations having these frequencies constitute the Stokes and anti-Stokes lines, respectively. The Raman shift, which is the difference in frequency between the incident and scattered radiation, should thus, according to the theory, be equal to the vibration frequency of the diatomic molecule.

It will be evident from the preceding discussion that the change of frequency in the scattered radiation, i.e., the Raman effect, is due to the variation of polarizability with time during the course of a vibration [equation (33.7)]. It will now be shown that it is also possible for rotation to be accompanied by a change in polarizability, and hence it can also give rise to Raman scattering. During the course of a rotation the orientation of a molecule with respect to the electric field of the radiation is changing; hence, if the molecule has different polarizabilities in different directions, that is, if it is *optically anisotropic*, its polarization will vary with time. By analogy with equation (33.7), the variation of the polarizability in the course of a rotation may be represented by an equation of the form

$$\alpha = \alpha_0 + \beta' \sin 2\pi(2\nu_r)t, \quad (33.9)$$

where ν_r represents the frequency of rotation. It will be noted that the quantity $2\nu_r$ is used in this expression, in place of ν_v in equation (33.7). The reason for the introduction of the factor 2 is that rotation of the diatomic molecule through an angle of π brings it into an orientation in which its polarizability is the same as initially. The polarizability thus changes at a rate that is twice as great as the rotation, and this leads to the result

given in equation (33.9). Combination of the latter with equation (33.4), then gives for the time variation of the induced dipole moment.

$$\begin{aligned}\mu &= \alpha_0 F_0 \sin 2\pi\nu t + \beta' F_0 \sin 2\pi\nu t \sin 4\pi\nu_r t \\ &= \alpha_0 F_0 \sin 2\pi\nu t + \frac{1}{2}\beta' F_0 \{\cos 2\pi(\nu - 2\nu_r)t - \cos 2\pi(\nu + 2\nu_r)t\}. \quad (33.10)\end{aligned}$$

According to this result the frequencies of the Raman lines should be $\nu - 2\nu_r$ for the Stokes lines, and $\nu + 2\nu_r$ for the anti-Stokes lines. The Raman shift should thus be equal to $2\nu_r$. Classically, all frequencies of rotation should exist in a gas at ordinary temperatures, and so the Raman spectrum should consist not of lines but of two continuous branches, one on each side of the incident radiation. However, the quantum theory indicates that only certain rates of rotation are possible, and the spectrum actually consists of a number of lines.

Apart from certain details, such as the one just mentioned, classical methods lead to a theory of the Raman effect which is in general agreement with experiment, as will be evident from the succeeding discussion. Before proceeding to a consideration of the conclusions to be drawn from the application of quantum mechanics, it is of interest to recall what is the fundamental cause of the frequency change in the scattered radiation. The classical treatment indicates that the vibrational Raman effect results from changes in polarizability in the course of vibration of a molecule, whereas the rotational Raman effect will occur only if the molecule is anisotropic, i.e., has different polarizabilities in different directions.

33c. Quantum Theory of the Raman Effect.—According to quantum theory, Rayleigh scattering is the result of the absorption of the incident radiation by the scattering molecules which are thereby raised to a higher energy state; on returning to their original state, radiation of the same frequency as that of the incident light is emitted. In the Raman effect, however, the molecules do not return to their original state, but to higher or lower vibrational or rotational levels; the frequency of the emitted (scattered) radiation is thus less or greater than that of the incident radiation by an amount equivalent to the difference in the vibrational or rotational energy states. The quantum theory of the Raman effect may thus be expressed in the following manner. Suppose the energy of a molecule in its initial (lower) state is represented by E'' , and it is exposed to incident radiation of frequency ν_i cm.⁻¹; the molecule is thus raised to a level in which its energy is $E'' + h\nu_i$. It then emits (scatters) radiation having the observed Raman frequency ν_s , and hence loses energy $h\nu_s$; in doing so it returns to a level of energy E' which lies above the E'' level; it follows, therefore, that

$$\begin{aligned}E'' + h\nu_i - h\nu_s &= E', \\ \therefore E' - E'' &= hc(\nu_i - \nu_s) \\ &= hc\Delta\nu. \quad (33.11)\end{aligned}$$

The energy change corresponding to the Raman shift, i.e., $hc\Delta\nu$, is thus equal to the difference in energy of the two levels represented by E' and E'' ,

respectively. If these are two different vibrational levels, then $\Delta\nu$ will clearly be approximately equal to, or a multiple of, the fundamental vibration frequency of the molecule. It is possible, also that E' and E'' may represent two rotational levels; in this case, $hc\Delta\nu$ will be related to the quantum of rotational energy.

In deriving equation (33.11) it was assumed that the molecule was initially in the state of lower energy, E'' . Under these conditions, $\nu_i - \nu_s$ is positive, and, as seen in Section 33a, the Stokes lines of the Raman spectrum are produced. If, however, the molecule is in the upper state E' when it takes up the energy of the incident light, and then returns to the lower state E'' after emission of the scattered Raman radiation, the energy changes may be represented by

$$\begin{aligned} E' + hc\nu_i - hc\nu_s &= E'', \\ \therefore E'' - E' &= hc(\nu_i - \nu_s) \\ &= hc\Delta\nu. \end{aligned} \quad (33.12)$$

In this case $\Delta\nu$ is negative, and so this condition gives rise to the anti-Stokes lines of the Raman spectrum.

The probability of the energy transitions involved in the Raman effect is determined by an expression of exactly the same form as equation (27.3). In the present case, however, μ_x represents the component of the *induced* dipole moment in the x direction; thus, utilizing equation (33.2), it is possible to write for the x component of the matrix element which determines the transition probability,

$$P_{mn(x)} = \int \psi_m^* (\alpha_{xx} F_x) \psi_n d\tau, \quad (33.13)$$

where α_{xx} is the polarizability in the x direction when the field F_x acts in the same direction. Assuming α_{xx} to vary in the course of an oscillation, in a manner similar to that given by equation (33.5), viz.,

$$\alpha_{xx} = \alpha_{xx}^0 + \beta_{xx} \frac{x}{A},$$

it follows that

$$P_{mn(x)} = F_x \alpha_{xx}^0 \int \psi_m^* \psi_n d\tau + \frac{F_x}{A} \beta_{xx} \int \psi_m^* x \psi_n d\tau. \quad (33.14)$$

The vibrational eigenfunctions are orthogonal, and hence the first term on the right-hand side of equation (33.14) is zero, except when m and n are equal; this term, therefore, gives rise to the radiation which does not involve a vibrational (or other) transition. That is to say, the first term represents the probability of the Rayleigh scattering. For Raman scattering, m and n will be different, and hence the first term in equation (33.14) is zero; the second term must, therefore, differ from zero if there are to be any Raman lines. It will be evident immediately that if β_{xx} is zero, the probability of

Raman scattering will also be zero; this means that the polarizability must vary during the course of the molecular vibration, otherwise there will be no Raman effect.

Similar considerations to the foregoing are applicable in the case of molecular rotation. It is evident from equation (33.13) that the polarizability, in either the x , y or z direction, must change in the course of a rotation, otherwise the transition probability will be zero and no Raman effect will be observed. It is necessary, therefore, for the molecule to be polarizable to different extents in different directions if it is to exhibit Raman scattering. The conclusions of this and the preceding paragraphs are identical with those reached in the classical treatment.

The polarizability of a molecule may be considered as made up of three components in directions at right angles; these give the dimensions of the so-called *polarization ellipsoid*. Provided there is a change in the polarizability in any one direction or, in other words, if any of the three dimensions of the polarization ellipsoid is changed, during the course of a molecular vibration, that vibration will interact with radiation to give a Raman effect. Similarly, provided the polarization ellipsoid is not spherical, i.e., if its three dimensions are not equal, then a rotational Raman effect will be possible. For a diatomic molecule, whether homonuclear or not, the polarizability ellipsoid will not be spherical and it will also change its dimensions in the course of a vibration; hence all such molecules exhibit both rotational and vibrational Raman spectra. It is only when there is no change in any of the polarizability components, that is, in any of the dimensions of the polarization ellipsoid, that no vibrational Raman effect is observed; this is the case with certain vibrations of polyatomic molecules, as will be seen subsequently. Similarly, spherically symmetrical molecules, such as methane and carbon tetrachloride, exhibit no rotational Raman effect.

It is of interest to call attention here to an important difference between classical and quantum theories in relation to the change of polarizability accompanying the vibration of molecules in their lowest ($v = 0$) level. According to classical theory, when the vibrational quantum number is zero, the molecule has no vibrational energy and hence does not oscillate. Molecules in their lowest levels should thus not be able to display vibrational Raman scattering. Experiment shows, however, that such molecules do actually exhibit the Raman effect, and the explanation of this fact is provided by quantum mechanics. According to the latter, molecules still possess a finite zero-point energy of vibration even in their lowest levels; the molecules can, effectively, never cease to vibrate. Raman scattering is thus possible for molecules, even when the vibrational quantum number is zero.

33d. Vibrational Raman Spectra.—If β_{xx} in equation (33.14), or one or other of the corresponding quantities in the y and z directions, is not zero, there will be Raman scattering, provided the integral in the second term of the equation differs from zero. This condition determines the selection rules for the levels m and n which combine to give the Raman shift. For a harmonic oscillator, it is found that the selection rule is the same as for

vibrational spectra, viz.,

$$\Delta v = \pm 1.$$

A Raman vibrational transition will thus occur only from one level to the next upper (Stokes) or to the next lower (anti-Stokes) level. At ordinary temperatures, as already seen, most of the molecules are in their lowest vibrational state, i.e., $v = 0$; hence the majority of transitions will be of the type $v = 0$ to $v = 1$. A small proportion of the molecules will initially occupy the $v = 1$ level, and these can undergo the Stokes transition, i.e., $v = 1$ to $v = 2$, or the anti-Stokes transition, i.e., $v = 1$ to $v = 0$. In either case, the intensities of the resulting lines must be low because of the small number of molecules involved. The vibrational Raman spectrum at ordinary temperatures should thus consist of one strong Stokes line, corresponding to the $v = 0$ to $v = 1$ transition; this may be accompanied by perhaps a further Stokes line and an anti-Stokes line of low intensity. These anticipations are in agreement with observation. At higher temperatures, the strength of the anti-Stokes line would be expected to increase, because of the increasing number of molecules that are initially in the higher vibrational levels.

The vibrational energy of a diatomic molecule, acting as an anharmonic oscillator, is given, as a first approximation, by equation (29.12), that is

$$E_v = (v + \frac{1}{2})hc\omega_e - (v + \frac{1}{2})^2hc x\omega_e.$$

For the strong line in the vibrational Raman spectrum, the quantum number v in the upper state is unity and in the lower state it is zero; using, as before, the symbols E' and E'' for the energies of the two states, it follows that

$$E' - E'' = (1 - 2x)hc\omega_e. \quad (33.15)$$

Utilizing equation (33.11), the Raman shift for the strong Stokes line will then be given by

$$\Delta\nu = (1 - 2x)\omega_e, \quad (33.16)$$

which is seen to be equal to the frequency of the center of the fundamental vibration band in the infra-red spectrum of the molecule [cf. equation (29.15)]. It is thus possible to verify the theory of the vibrational Raman effect by comparison of the frequencies of the infra-red bands with the Raman shifts. For an unsymmetrical diatomic molecule the vibration spectrum and the Raman effect are both active and capable of direct measurement. If the molecule is symmetrical, and has no resultant dipole moment, there is no infra-red spectrum, but the value of $(1 - 2x)\omega_e$ can be calculated from data derived from the electronic band spectrum. The Raman shift can be observed in any case, as the polarizability changes during vibration. A comparison of the Raman vibrational shifts with the calculated or observed values of $(1 - 2x)\omega_e$, for a number of symmetrical and unsymmetrical diatomic molecules, are given in Table XII; the agreement is seen to be very satisfactory.

The selection rule $\Delta v = \pm 1$ is strictly applicable only to a harmonic oscillator; if the vibrations are anharmonic in character, overtones for which Δv is 2, 3, etc., become possible theoretically. Such overtones, if they are observed at all, will be very faint. Their frequencies will be given by equa-

TABLE XII. COMPARISON OF RAMAN AND VIBRATIONAL EFFECTS

Molecule	Raman Shift	Vibration Frequency
Hydrogen chloride	2886 cm. ⁻¹	2885.9 cm. ⁻¹
Hydrogen bromide	2558	2559.3
Hydrogen iodide	2233	2230
Nitric oxide	1877	1879
Carbon monoxide	2145	2144
Hydrogen	4156	4154.6*
Nitrogen	2331	2330.7*
Oxygen	1555	1556.2*

* Calculated from electronic spectra.

tion (29.14), since the great majority of the molecules are initially in their lowest ($v = 0$) level. If the Raman frequency shift of the overtone, as well as that of the fundamental, could be determined it would be possible to calculate both ω_e and x for the given molecule. The frequency shift corresponding to the transition $v = 0$ to $v = 1$ gives $(1 - 2x)\omega_e$, and from this alone it is not possible to evaluate separately the equilibrium vibration frequency and the anharmonicity constant.

An isotope effect should be observed in vibrational Raman spectra, just as in other forms of vibrational spectra. If $\Delta\nu_1$, and $\Delta\nu_2$ are the Raman displacements for two isotopic molecules, then by equation (33.16),

$$\Delta\nu_1 = (1 - 2x_1)\omega_1$$

and

$$\Delta\nu_2 = (1 - 2x_2)\omega_2.$$

Making use of the relations given earlier, that

$$\omega_2 = \rho\omega_1 \quad \text{and} \quad x_2 = \rho x_1,$$

it follows that

$$\frac{\Delta\nu_1}{\Delta\nu_2} = \left(\frac{1 - 2x_1}{1 - 2\rho x_1} \right) \frac{1}{\rho}.$$

Since x is small, the quantity in the parentheses will not be appreciably different from unity; hence,

$$\frac{\Delta\nu_1}{\Delta\nu_2} = \frac{1}{\rho} = \left(\frac{\mu_2}{\mu_1} \right)^{1/2}, \quad (33.17)$$

where μ_1 and μ_2 are the reduced masses of the isotopic molecules.

The simplest case in which the isotope effect has been studied is that of the three isotopic molecules H_2 , HD and D_2 ; the observed frequency shifts are 4156, 3631 and 2992 cm.⁻¹, respectively, so that the ratios are 1.39 to

1.21 to 1.00. The corresponding ratios of the square roots of the reduced masses are 1.41 to 1.22 to 1.00.

33e. Rotational Raman Spectra.—The selection rule for rotational Raman transitions differs from that for purely rotational changes; for the Raman effect it is

$$\Delta J = 0, \pm 2$$

for diatomic molecules in Σ states, i.e., when Λ is zero.¹² The fact that ΔJ can be equal to ± 2 is equivalent to the classical result of Section 33b, that the frequency of the scattered light is changed by the amount $2\nu_r$. When ΔJ is zero, the scattered Raman radiation has the same frequency as the incident light, and so there is no Raman shift; the Raman line is then indistinguishable from the spectral line due to the incident light or to Rayleigh scattering. The only Raman shifts that can be observed for Σ molecules are those corresponding to the transitions $\Delta J = +2$ (Stokes lines) and $\Delta J = -2$ (anti-Stokes lines). Since rotational quanta are relatively small, a considerable number of energy levels will be occupied by many molecules at ordinary temperatures. Hence, several rotational Raman transitions, with J initially equal to 0, 1, 2, etc., up to 10 or more, will be observed. Utilizing equation (28.1) for the energy of a rigid rotator

$$E_r = \frac{h^2}{8\pi^2 I} J(J+1),$$

it follows that for $\Delta J = +2$, the values of the rotational Raman shifts of the Stokes lines will be given by

$$\begin{aligned} \Delta\nu &= \frac{h}{8\pi^2 I_c} \{ (J+2)(J+3) - J(J+1) \} \\ &= 2B(2J+3), \end{aligned} \tag{33.18}$$

where B is defined, as previously, as $h/8\pi^2 I_c$. An exactly similar expression, but of opposite sign, may be derived for the frequency shifts of the anti-Stokes rotational lines, so that it is possible to write

$$\Delta\nu = \pm 2B(2J+3), \quad \text{where} \quad J = 0, 1, 2, \dots \tag{33.19}$$

The numerical value of the frequency separation of successive lines in the Raman rotational spectrum is seen to be equal to $4B$, as compared with $2B$ for other rotational spectra; this difference is, of course, due to the change of two units in the rotational quantum number in the Raman effect, as compared with unity in the infra-red and electronic spectra. For hydrogen chloride the separation of the rotational Raman lines is approximately 41.6 cm.^{-1} , which may be compared with 20.7 cm.^{-1} for the infra-red and 21.2 cm.^{-1} for electronic spectra.

¹² For diatomic molecules in other than Σ states, i.e., Λ is not zero, the theoretical selection rule is $\Delta J = 0, \pm 1, \pm 2$. The only case in which this might arise is nitric oxide.

It should be noted that the displacement of the first lines ($J = 0$) on each side of the exciting line is larger than the other frequency separations of $4B$; if J in equation (33.19) is put equal to zero, the Raman shift is seen to be $6B$. It follows, therefore, that the rotational Raman spectrum will thus consist of two series of lines (Stokes and anti-Stokes), one set on each side of the exciting line. The first line will, in each case, be displaced by a frequency of $6B$, the subsequent lines being separated by $4B$. Experimental results bear out these anticipations.

The foregoing calculations have been based on the approximation that the diatomic molecule behaves as a rigid rotator. If the more complete form of the expression for the rotational energy [equation (28.9)] is employed, the equation for the Raman shift becomes

$$\Delta\nu = \pm \{ (2B - 4D(J^2 + 3J + 3)) (2J + 3) \}. \quad (33.20)$$

This reduces, of course, to equation (33.19) when D is negligibly small; in any event, D is of the order of $10^{-4}B$, and hence it may be ignored provided J is not large.

For symmetrical molecules, there are further restrictions in connection with the permitted Raman transitions, just as in the case of the rotational changes that accompany electronic transitions (Section 31d). Because of the great difficulty of reversing nuclear spins, symmetric rotational levels will combine with symmetric levels, and antisymmetric with antisymmetric levels. The selection rule

$$s \leftrightarrow s \quad \text{and} \quad a \leftrightarrow a,$$

therefore, applies equally to the Raman effect as to other changes involving rotational transitions. When the positive and negative character of the levels for Σ states is under consideration, however, the selection rule for Raman spectra is different from that applicable to rotational changes in electronic spectra. The proper rule can be readily derived from an examination of the x component of the matrix element which determines the transition probability between two energy levels indicated by the letters m and n ; for the Raman effect this can be written in the form of equation (33.13), viz.,

$$P_{mn(x)} = F_x \int \psi_m^* \alpha_{xx} \psi_n d\tau.$$

If m and n refer to rotational levels and they are both positive, reflection at the origin (inversion) will not alter the signs of the eigenfunctions ψ_m^* and ψ_n ; further, since the polarizability α_{xx} of the molecule is the same in the two directions, the sign of α_{xx} will also be unchanged. The integrand will thus remain unaffected by the inversion, and hence it can differ from zero. If one of the rotational levels is positive while the other is negative, the sign of the integrand must change upon inversion, and since the value of a definite integral must be independent of any transformation of the coordinates, it

must in this case be equal to zero (cf. Section 31d). It follows, therefore, that in the Raman effect the permitted transitions are

$$+\leftrightarrow+ \quad \text{and} \quad -\leftrightarrow-,$$

while the transitions between positive and negative rotational states are forbidden.

An examination of Table XI shows that these selection rules are in harmony with the rule that ΔJ is zero or ± 2 . Remembering that the resultant rotational transitions in the Raman effect occur within the same electronic state, it is seen that for molecules with Σ terms, at least, a change in the value of J by zero or by two units, must lead to the combinations $s \leftrightarrow s$ and $a \leftrightarrow a$, and $+\leftrightarrow+$ and $-\leftrightarrow-$. No other transitions can occur if ΔJ is restricted in this manner. Similar results are obtained for molecules in electronic states other than Σ states, and so the rules are of general applicability.

Because of the restriction concerning transitions between symmetric and antisymmetric rotational levels, the Raman spectrum of homonuclear molecules should show the phenomenon of varying intensities of alternate rotational lines, just as in the electronic spectra of these substances. If the nuclear spin is zero, alternate lines should be missing; such is actually the case in the rotational Raman band of molecular oxygen $^{16}\text{O}^{16}\text{O}$. If the even rotational levels, i.e., with $J = 0, 2, 4$, etc., are missing, the first observed rotational line is that for $J = 1$, and the frequency shift, as given by equation (33.18), is equal to $10B$, as compared with $6B$ if there are no missing lines. The frequency separations of successive lines should be $8B$, if alternate lines are absent, compared with $4B$ if all the lines are present. On the other hand, if the odd lines, $J = 1, 3, 5$, etc., are missing, the frequency shift of the first observed line ($J = 0$) will be $6B$, but the separation of successive lines will still be $8B$. The ratio of the frequency displacement of the first observed rotational Raman line to the frequency separation of successive lines, will thus be as follows:

	Ratio
Even J values missing	5 : 4
No missing levels	3 : 2
Odd J values missing	3 : 4

From a study of the Raman spectrum of molecular oxygen it is observed that the ratio is 5 : 4, and hence the rotational levels for which J has even values are missing. The same conclusion has been reached from an examination of the electronic spectra, as mentioned earlier.

If the intrinsic angular momentum (spin) of the two nuclei is not zero, then alternate lines in the rotational Raman spectrum of a homonuclear diatomic molecule should not be absent entirely, but should exhibit an alternation of intensity. Such alternations have been clearly observed in the Raman spectra of symmetrical molecules of hydrogen, deuterium and

nitrogen. With hydrogen deuteride, which does not have two identical nuclei, all rotational lines have equal intensities and none are missing.

33f. Vibration-Rotation Raman Spectra.—It is theoretically possible for vibrational and rotational transitions to occur simultaneously in a Raman transition; the selection rules are identical with those for the separate transitions, viz., $\Delta v = \pm 1$ and $\Delta J = 0, \pm 2$. Since it is possible for ΔJ to be zero, a Raman line representing the Q branch should be observed. The frequency of this line, which will be referred to as $\Delta\nu_0$, is, of course, identical with that for the pure vibrational transition. Because of the difference in the moments of inertia in the two vibrational levels, the Q branch should actually consist of a number of closely spaced lines (Section 29e). However, only for hydrogen, which has a very small moment of inertia, has it been found possible to resolve the constituent lines of the Q branch. The fine structures undoubtedly exist in all other cases, but so far they have not been resolved. It should be noted that diatomic molecules, which do not normally possess Q branches in their vibration spectra, have Q branches in their Raman spectra.

If, as a first approximation, it is assumed that vibrational and rotational energies are additive, the frequencies of the vibration-rotation Raman lines can be readily derived from results already obtained. If $\Delta\nu_0$ is the frequency shift for the purely vibrational transition (Q branch), the Raman displacements for the accompanying rotational transitions will be given by

$$\Delta J = +2: \Delta\nu = \Delta\nu_0 + 2B(2J + 3), \quad \text{where } J = 0, 1, 2, \dots, \quad (33.21)$$

and

$$\Delta J = -2: \Delta\nu = \Delta\nu_0 - 2B(2J + 3), \quad \text{where } J = 0, 1, 2, \dots \quad (33.22)$$

The central vibrational Raman lines (Q branch) will thus be accompanied by two wings or branches, each consisting of a set of fairly closely spaced rotational lines. Since the lines of the Q branch fall almost in the same position for all J values, whereas those in the two wings are separated, it is clear that the central line will be much more intense than the lines constituting the wings. The branch on the low frequency side for which ΔJ is -2 is known as the O branch, while that on the high frequency side for which ΔJ is $+2$ is called the S branch. This nomenclature is employed so that the series O , P , Q , R and S branches refers to ΔJ values of -2 , -1 , 0 , $+1$ and $+2$, respectively. Normally, the vibration-rotation Raman spectrum of a diatomic molecule has O , Q and S branches, but for electronic states other than Σ states, i.e., if Λ is not zero, P and R branches are also possible, since the transitions for which ΔJ is ± 1 are permitted. The only diatomic molecule for which this might be observed is nitric oxide, but the multiplicity of the lines makes the bands difficult to resolve.

33g. Form of Raman Spectra.—From the results of the preceding sections, it is possible to derive a fairly complete picture of the Raman spectra. Since the frequency displacements for rotational transitions are small in-

tegral multiples of B , while for vibrational transitions they are of the order of the vibration frequency of the molecule, it is evident that rotational Raman shifts are much smaller than the vibrational shifts. It follows, therefore, that the Raman spectrum will consist, first, of a very intense line, representing the incident light and that due to Rayleigh scattering. At each side of, and close to, this line will be found the Stokes and anti-Stokes lines, respectively, of almost equal intensity, corresponding to various rotational transitions. At a greater distance from the exciting line, on the low frequency side, there will be a relatively strong (Stokes) line for the Q branch ($\Delta J = 0$) of the vibrational transition $v = 0$ to $v = 1$; on each side of this line, and close to it, there may be observed fainter lines of the O and S branches for ΔJ equal to -2 and $+2$, respectively. There is the possibility that an anti-Stokes Q branch will appear at an equal frequency distance on the high frequency side of the exciting line, but this will be very faint at ordinary temperatures.

As already indicated, the data relating to molecular vibration and rotation obtained from Raman spectra are in satisfactory agreement with those derived from the infra-red and electronic bands. Since even symmetrical molecules exhibit Raman scattering, information can thus be obtained from the Raman effect, which otherwise could be determined only from electronic spectra. The values of vibration frequencies and moments of inertia calculated from the latter are more accurate, and so Raman spectra of diatomic molecules are not of great practical importance. The results for such molecules, however, serve to confirm the fundamental theory of Raman scattering. For polyatomic molecules, on the other hand, the Raman effect plays an important part. The electronic spectra of such molecules are so complex, and often so badly defined, that little information can be obtained from them. The Raman spectra of polyatomic molecules provide data, supplementing those derived from infra-red spectra, that have proved invaluable in many cases, as will be seen later.

CHAPTER V

MOLECULAR SPECTRA: POLYATOMIC MOLECULES ¹

MOLECULAR VIBRATIONS

34a. Normal Coordinates.²—In view of the fact that little progress has been made in the analysis of the electronic spectra of polyatomic molecules, the treatment of such molecules will be restricted here to infra-red and Raman spectra. From both of these, results of chemical interest have been obtained. An essential step in the study of the spectra of polyatomic molecules is the purely mechanical problem of vibrational modes, and this will be considered first. A molecule consisting of n atoms will, in general, have $3n - 6$ degrees of vibrational freedom,³ and hence $3n - 6$ coordinates are required to specify the vibrational state of the molecule. If the number $3n - 6$ is represented by s , then there may be chosen a set of coordinates, $q_1, q_2, \dots, q_i, \dots, q_s$, which give the displacements of the atoms from their equilibrium positions as a result of vibration. In other words, the q 's may be regarded as giving the coordinates of each atomic nucleus, referred to the equilibrium position of that nucleus as the origin. As seen in Section 29b, the potential energy may be expanded in the form of a Taylor series in terms of these coordinates; for small vibrations, all terms beyond the quadratic may be neglected, so that equation (29.9) reduces to the form

$$V = \frac{1}{2} \sum_{ij} b_{ij} q_i q_j \quad (34.1)$$

where b_{ij} is defined by

$$b_{ij} = \left(\frac{\partial^2 V}{\partial q_i \partial q_j} \right)_0.$$

If equation (34.1) for the potential energy is written out in full, it becomes

$$V = \frac{1}{2} (b_{11} q_1^2 + b_{22} q_2^2 + \dots + 2b_{12} q_1 q_2 + 2b_{13} q_1 q_3 + \dots + 2b_{23} q_2 q_3 + \dots). \quad (34.2)$$

¹ Bhagavantam, "Scattering of Light and the Raman Effect"; Hibben, "The Raman Effect and its Chemical Applications"; Kohlrausch, "Der Smekal-Raman Effekt," and the "Ergänzungsband, 1931-37"; Kronig, "Optical Basis of the Theory of Valency"; Sponer, "Molekülspektren"; Sutherland, "Infra-Red and Raman Spectra"; *Ann. Reports Chem. Soc.*, 32, 53 (1935); 33, 53 (1936); 35, 37 (1938); Thompson, *ibid.*, 38, 46, 60 (1941); Wu, "Vibrational Spectra and Structures of Polyatomic Molecules."

² Whittaker, "Analytical Dynamics"; see also, Pauling and Wilson, "Introduction to Quantum Mechanics," p. 282 et seq.

³ Linear molecules have $3n - 5$ degrees of vibrational freedom. If there is internal rotation in any molecule, the number of degrees of vibrational freedom is reduced by one for every degree of free internal rotation.

The kinetic energy T can be expressed by means of a similar equation,

$$T = \frac{1}{2}(a_{11}\dot{q}_1^2 + a_{22}\dot{q}_2^2 + \cdots + 2a_{12}\dot{q}_1\dot{q}_2 + 2a_{13}\dot{q}_1\dot{q}_3 + \cdots + 2b_{23}\dot{q}_2\dot{q}_3 + \cdots) \quad (34.3)$$

$$= \frac{1}{2} \sum_{ij} a_{ij} \dot{q}_i \dot{q}_j, \quad (34.4)$$

where the a_{ij} terms are functions of the masses of the atoms constituting the polyatomic molecule.

The Lagrange equation of motion is

$$\frac{d}{dt} \left(\frac{\partial L}{\partial \dot{q}_k} \right) - \frac{\partial L}{\partial q_k} = 0, \quad (34.5)$$

where L is the Lagrangian function, or kinetic potential, equal to $T - V$. In the present case, the kinetic energy T is a function of the velocities \dot{q}_k only, whereas the potential energy V is a function of the coordinates q_k only; hence equation (34.5) may be written as

$$\frac{d}{dt} \left(\frac{\partial T}{\partial \dot{q}_k} \right) + \frac{\partial V}{\partial q_k} = 0, \quad \text{where } k = 1, 2, 3, \dots, s. \quad (34.6)$$

Differentiation of equations (34.1) and (34.4) with respect to \dot{q}_k and q_k , respectively, and insertion of the results into equation (34.6) gives a series of s equations of the general form

$$\sum_j (a_{jk}\ddot{q}_j + b_{jk}q_j) = 0, \quad (34.7)$$

with k taking one of the values $1, 2, 3, \dots, s$. For such equations, a general solution will be

$$q_k = A_k \sin(\sqrt{\lambda}t + \alpha). \quad (34.8)$$

It will be noted that this equation is one that is characteristic of wave motion, with amplitude A_k and phase constant α ; the frequency ν is then related to the quantity λ by

$$\lambda = 4\pi^2\nu^2. \quad (34.9)$$

If the value of q_k given by equation (34.8) is substituted in (34.7), there will be obtained s equations of the type

$$\sum_j (b_{jk} - a_{jk}\lambda) A_j = 0. \quad (34.10)$$

This gives a set of s simultaneous, linear, homogeneous equations in the A 's, and if they are to have nontrivial solutions, i.e., the A 's are not all to be

zero, it follows that

$$\begin{vmatrix} b_{11} - a_{11}\lambda & b_{12} - a_{12}\lambda & b_{13} - a_{13}\lambda & \cdots & b_{1s} - a_{1s}\lambda \\ b_{21} - a_{21}\lambda & b_{22} - a_{22}\lambda & b_{23} - a_{23}\lambda & \cdots & b_{2s} - a_{2s}\lambda \\ b_{31} - a_{31}\lambda & b_{32} - a_{32}\lambda & b_{33} - a_{33}\lambda & \cdots & b_{3s} - a_{3s}\lambda \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ b_{s1} - a_{s1}\lambda & b_{s2} - a_{s2}\lambda & b_{s3} - a_{s3}\lambda & \cdots & b_{ss} - a_{ss}\lambda \end{vmatrix} = 0. \quad (34.11)$$

This secular determinant is an equation of the s th degree, giving s values for λ in terms of the a 's and b 's. The ratio of the A_k 's can now be determined by the method described in Section 14c for the evaluation of the coefficients of the eigenfunctions in the variation procedure.

Returning to a consideration of the coordinates, namely the q 's, it is always possible to make a linear transformation of them, viz.,

$$q_k = \sum_{l=1}^s c_{kl} Q_l, \quad (34.12)$$

which permits the elimination of all cross-product terms from the expressions, equations (34.1) and (34.4), for the potential and kinetic energies; these may then be written as

$$V = \frac{1}{2} \sum_l \lambda_l Q_l^2 \quad (34.13)$$

and

$$T = \frac{1}{2} \sum_l \dot{Q}_l^2. \quad (34.14)$$

This procedure is generally referred to as a *normal coordinate* transformation. The appropriate form of the Lagrange equation (34.6) is now

$$\frac{d}{dt} \left(\frac{\partial T}{\partial \dot{Q}_l} \right) + \frac{\partial V}{\partial Q_l} = 0, \quad \text{where} \quad l = 1, 2, 3, \dots, s,$$

and since the expressions for T and V contain no cross terms, and the a 's are all unity, the set of s equations corresponding to (34.7) now take the form

$$\ddot{Q}_l + \lambda_l Q_l = 0.$$

The solution can be written as

$$Q_l = B_l \sin(\sqrt{\lambda_l} t + \beta), \quad (34.15)$$

where B_l is now the amplitude referred to the normal coordinates. Since q_k is a linear combination of the Q_l 's, it can be shown by a comparison of equations (34.15) and (34.8) that the λ 's in the two equations are identical.

The ratio of the B_l 's with respect to one of them can be determined in the usual manner, as mentioned above in connection with the A_k 's.

Further, in view of equation (34.12), it is possible to represent A_k of equation (34.8) as a linear function of the B_l 's, so that

$$A_k = \sum_{l=1}^s c_{kl} B_l, \quad (34.16)$$

and since the A_k 's and the B_l 's, or rather their ratios with respect to one of them in each case, are known, it is possible to determine the ratio of the c_l 's for each k value. With this information concerning the coefficients in equation (34.12), it is possible to carry out the transformation from the arbitrary (q_k) to the normal (Q_l) coordinates.

If the value of Q_l given by equation (34.15) is inserted into equation (34.12), it is found that

$$q_k = \sum_{l=1}^s c_{kl} B_l \sin(\sqrt{\lambda_l} t + \beta). \quad (34.17)$$

Suppose the molecule under consideration is made to vibrate in such a way that all the amplitudes B_l , except one, namely B_1 , are zero; in other words, suppose all the terms in the summation, except that with $l = 1$, are zero, then

$$q_{k(1)} = c_{k1} B_1 \sin(\sqrt{\lambda_1} t + \beta_1) \quad (34.18)$$

with

$$k = 1, 2, 3, \dots, s.$$

This result shows that all the nuclei of the molecule undergo simple harmonic motion with a frequency ν_1 , which is related to λ_1 , by

$$\lambda_1 = 4\pi^2 \nu_1^2,$$

and that all the vibrations are in the same phase. In other words, it appears that the n nuclei constituting the molecule vibrate in such a manner that they all pass through their equilibrium positions simultaneously, and also attain their maximum amplitudes simultaneously. Although the vibration frequencies and phase constants for all the nuclei are the same, the amplitudes which are equal to $c_{k1} B_1$, will depend on k , and hence will vary from one nucleus to another. A vibration of the type that satisfies the requirements of equation (34.18), namely, that all the nuclei vibrate in phase and with the same frequency, is said to be a *normal vibration* of the molecule.

It is apparent that according to equation (34.17) the molecule will possess s , generally equal to $3n - 6$, such normal (or fundamental) modes of vibration, for a result equivalent to equation (34.18) will be obtained by keeping all the B_l 's equal to zero, with the exception of B_1, B_2 , etc., in turn. There will thus be s values of the frequencies ν of the normal vibrations, given by the general equation

$$\lambda = 4\pi^2 \nu^2, \quad (34.19)$$

where the λ 's are the s solutions of the determinantal equation (34.11). It follows, therefore, that if the kinetic and potential energies of a vibrating molecule are expressed in the forms of equations (34.2) and (34.3), so that the a_{ij} 's and b_{ij} 's are known, it is possible to evaluate the λ 's; hence the normal vibration frequencies of the molecule can be derived from equation (34.19). It may be noted that in certain cases two or more normal vibrations will have the same frequency; such vibrational modes are said to be *degenerate*. In general, vibrational degeneracy is the result of molecular symmetry, although there is the phenomenon of accidental degeneracy due to other causes (Section 37).

In the foregoing discussion the treatment has been simplified by taking all the B_i 's except one to be zero; however, in the most general case the displacement q_k is given by equation (34.17), and this obviously represents the summation of the displacements due to the separate normal vibrations. It is seen, therefore, that no matter how complex the actual vibrational motion of the molecule may be, it can be treated as equivalent to the superposition of the $3n - 6$ separate, relatively simple, normal vibrations associated with that particular molecule. There are several important aspects of the subject of normal vibrations which have a bearing on the problems of molecular spectra, and some of these will be referred to below.

34b. Normal Vibrations and Vibrational Energy.—The wave equation for the motion of the *nuclei* of a molecule can be put in the form

$$\frac{h^2}{8\pi^2 m_i} \sum \nabla_i^2 \psi + (E - V)\psi = 0, \quad (34.20)$$

where m_i refers to the mass of the i th nucleus, and ψ is the nuclear wave function. If the Laplacian operator is expressed in terms of the coordinates q_k , it follows that equation (34.20) may be written as

$$\frac{h^2}{8\pi^2} \sum_{k=1}^s \frac{1}{m_k} \cdot \frac{\partial^2 \psi}{\partial q_k^2} + (E - V)\psi = 0, \quad (34.21)$$

and if the transformation is made to normal coordinates, as described in Section 34a, so that the potential and kinetic energies are given by equations (34.13) and (34.14), respectively, equation (34.21) becomes

$$\frac{h^2}{8\pi^2} \sum_{i=1}^s \frac{\partial^2 \psi}{\partial Q_i^2} + (E - \frac{1}{2} \sum_{i=1}^s \lambda_i Q_i^2) \psi = 0. \quad (34.22)$$

If the nuclear wave function ψ is expressed as a product of s eigenfunctions, each of which is a function of one of the Q 's, viz.,

$$\psi = \psi_1(Q_1)\psi_2(Q_2)\psi_3(Q_3) \cdots \psi_s(Q_s), \quad (34.23)$$

then it is possible to separate equation (34.22) into s independent equations

of the form

$$\frac{h^2}{8\pi^2} \cdot \frac{\partial^2 \psi_j}{\partial Q_j^2} + (E_j - \frac{1}{2}\lambda_j Q_j^2)\psi_j = 0, \quad (34.24)$$

each being associated with one of the normal coordinates. It will be observed by comparison with equation (8.9) that this expression is identical in form with that for a one-dimensional harmonic oscillator; the eigenvalues of the vibrational energy E_j for the j th normal coordinate are consequently given by

$$E_j = (v_j + \frac{1}{2})h\nu_j, \quad (34.25)$$

where v_j is the vibrational quantum number, equal to 0, 1, 2, etc., and ν_j is the classical frequency, in wave numbers, of the j th normal vibration. The total vibrational energy E_v of the molecule is equal to the sum of the energies E_j associated with the s separate normal coordinates; thus,

$$E = \sum_{j=1}^s E_j = \sum_{j=1}^s (v_j + \frac{1}{2})h\nu_j$$

or

$$E = (v_1 + \frac{1}{2})h\nu_1 + (v_2 + \frac{1}{2})h\nu_2 + \cdots + (v_s + \frac{1}{2})h\nu_s. \quad (34.26)$$

It is evident from this result that a polyatomic molecule can have many vibrational energy levels, and hence the vibration spectrum is likely to be complex. In the simplest case, however, when the value of v_j for a given normal vibration changes by unity, the frequency of the corresponding spectral line will be ν_j . It follows, therefore, that if all the vibrational modes were spectroscopically active, the frequencies of the fundamental vibration bands, for which $\Delta v_j = 1$, would be equal to the $3n - 6$ classical normal vibration frequencies of the molecule. In practice the situation is complicated by the fact that not all the frequencies are active, by the presence of spectral lines due to overtones, i.e., when $\Delta v_j > 1$, and by the formation of combination tones when changes occur simultaneously in two or more of the v_j 's. In spite of these difficulties, the general nature of the conclusions to be drawn from the foregoing treatment is of great importance. No matter how involved may be the actual vibration of the nuclei in a given molecule, the frequencies of the fundamental lines in the vibration spectrum, disregarding overtones, combination tones and missing lines, will be equal to the normal vibration frequencies of that molecule.

Although the arguments presented above were based on the approximation of harmonic oscillation, involving the neglect of all terms beyond the quadratic in the Taylor series for the potential energy, the same general results can be derived for an anharmonic oscillator. The only essential difference is that the frequencies of the vibrational lines are not exactly equal to the normal vibration frequencies of the molecule, just as is the case with diatomic molecules (cf. Section 29b). It is possible, however, in many instances to derive the correction terms involving the anharmonicity constants, but the treatment will not be given here.

34c. Nature of Normal Vibrations.—For the further consideration of the results of molecular spectra of polyatomic molecules, it is desirable to know something concerning the nature of the nuclear motions associated with each normal vibrational mode of a given molecule. In principle, the procedure that must be adopted to acquire this information is based on the discussion in Section 34a; the expressions for the potential and kinetic energies are written out in terms of the displacements of the atomic nuclei from their equilibrium positions, with reference to a convenient system of coordinates. By solving the secular equation (34.11), and carrying out the subsequent calculations, as already described, it is possible to determine the coefficients c_{kl} , by means of which the arbitrarily chosen coordinates q_k are transformed into the normal coordinates Q_l [equation (34.12)]. It is then a relatively simple matter to perform the inverse transformation, so that the coefficients c' of the relationship

$$Q_l = \sum_k c'_{kl} q_k \quad (34.27)$$

can be evaluated. In this way it is possible to determine the forms of the displacements, in terms of the chosen coordinates, that correspond to the normal vibrations.

The nature of the results may be illustrated by reference to the simple case of the symmetrical triangular molecule YX_2 (Fig. 26). The displacements of the three atoms may be represented by means of the coordinates x , y and q ; x is the relative displacement from the symmetry axis of the atom Y , in the plane of the molecule; y is the relative displacement of Y with respect to the mass center of the two X atoms, and q is the relative displacement of the X atoms along the line joining them. By carrying out the normal coordinate treatment, the expressions giving the displacements Q_1 , Q_2 and Q_3 , in the directions of the three normal coordinates, since $3n - 6$ is now equal to three, are

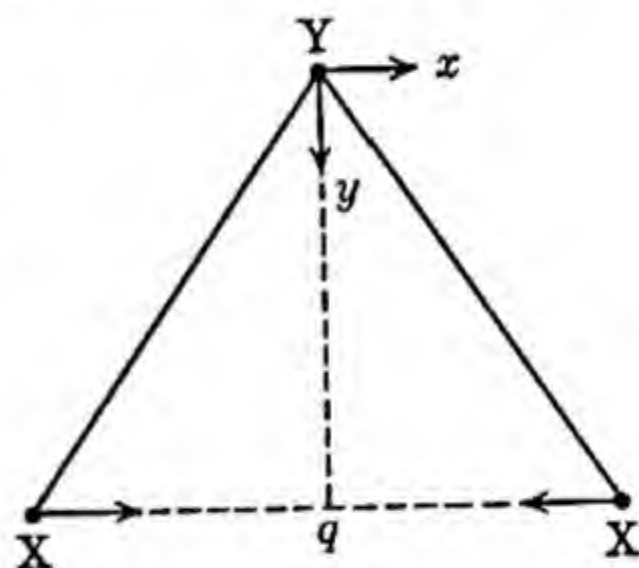


FIG. 26. Coordinates of YX_2 molecule

$$\begin{aligned} Q_1 &= a_1 y + b_1 q \\ Q_2 &= a_2 y - b_2 q \\ Q_3 &= cx. \end{aligned}$$

These results mean that in the first two normal vibrations, having frequencies ν_1 and ν_2 , there is no displacement of the atom Y in the x direction; in both cases, however, there are y and q displacements, but in one normal vibration the q displacement is in the opposite direction to that in the other. Finally, the third normal vibration, of frequency ν_3 , is characterized by a displacement of the atom Y in the x direction alone; there is no resultant displacement in the q direction, so that the X atoms remain at a fixed distance apart in the course of their motion. These conditions are evidently satisfied

by the motions represented in Fig. 27; the diagrams may be taken as giving an approximate picture of the nature of the normal vibrations of a symmetrical triangular molecule, such as H_2O , D_2O , H_2S , D_2S , SO_2 , etc. The actual vibrational motion of the YX_2 molecule will be complicated, but no matter how complex it is, it can be treated as equivalent to the superposition of the three types of oscillation shown in Fig. 27. It will be recalled that

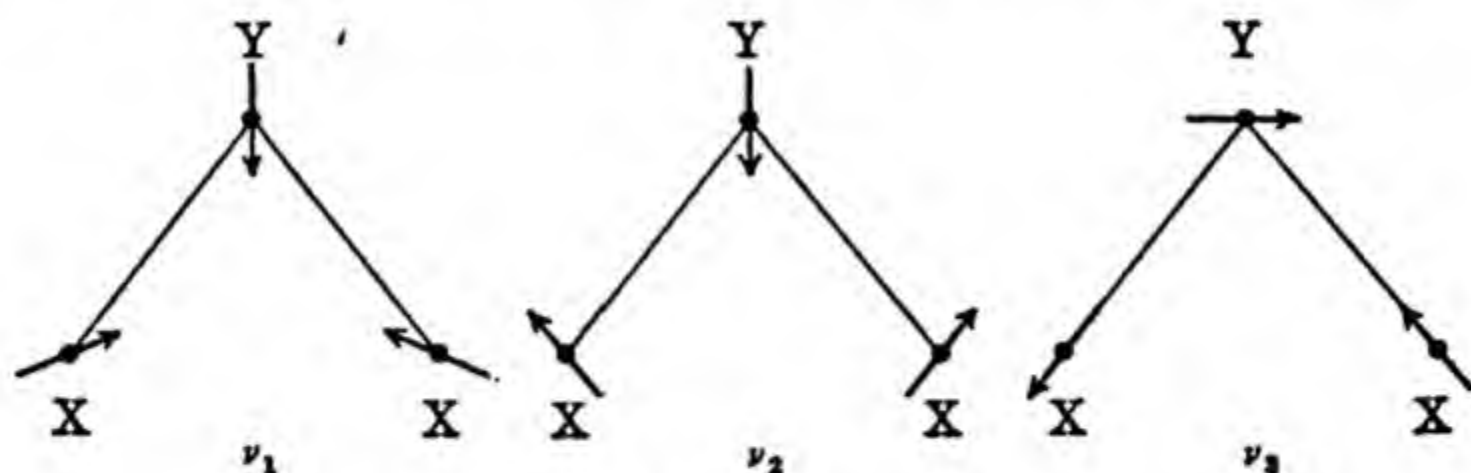


FIG. 27. Normal vibrations of YX_2 molecule

in each of the normal vibrations the nuclei of the three atoms will be moving in phase, in the directions of the arrows, although the amplitudes of vibration may be different for the three nuclei.

The normal coordinate treatment of an angular triatomic molecule involves the solution of a third order determinant. For a linear molecule containing three atoms, there are actually four normal vibrations, and the determinant will be of the fourth order, although two of the solutions are identical, as will be explained shortly. When the molecule contains four or more atoms, the direct solution of the normal coordinate problem becomes almost impossibly difficult. Fortunately, however, a remarkable simplification has resulted from the ingenious application of the branch of mathematics known as *group theory*. By making use of the symmetry properties of the molecule, it is possible to choose the coordinates (symmetry coordinates) in such a manner that both the kinetic and potential energies can be separated into parts, there being no cross terms between coordinates involved in one part with those in any other part. The coordinates concerned in each part have the same symmetry characteristics, but different from those in the other parts. The result of this separation is that the secular equation from which the λ 's are obtained is immediately factorized into a number of equations of lower degree; each of these equations involves one set only of the separated coordinates with the same symmetry.

The symmetry of the molecule identifies the particular group, analogous to a crystallographic space group, to which the molecule belongs, and each such group is associated with a specific number of *irreducible representations*. Each of the latter represents a type of symmetry for the normal coordinates of the molecule of the particular group. Every one of the normal coordinates must, in fact, belong to a symmetry which is correlated with one of the irreducible representations of the given group. If there is more than one normal coordinate possessing the same symmetry, the corresponding

irreducible representation will appear the appropriate number of times in the complete representation of the group. The determinantal equation (34.11) is thus factorized into a number of determinants equal to the number of irreducible representations of the group; the order of each of these determinants is equal to the number of times the corresponding irreducible representation occurs in the complete representation. Consider, for example, a symmetrical pyramidal molecule YX_3 , such as NH_3 , PCl_3 , etc.; this belongs to the group C_{3v} , with which are known to be associated two different irreducible representations for the normal vibrations. Each of these two irreducible representations appears twice in the complete representation of the C_{3v} group, one of them being doubly degenerate; this means that there are effectively three irreducible representations, but two are identical. Since each of these representations appears twice in the complete group, it follows that the sixth order determinant which must be solved for the YX_3 molecule, since there are six vibrational modes, is reduced, by the proper choice of the coordinates, to three quadratics, two of which are identical. The solution of the problem is thus enormously simplified.

The methods of group theory have been applied to molecules of various types of symmetry, and from the tabulated results it is possible to obtain the information which permits the immediate classification of the normal vibrations of most molecules that are not too complex. With the information so obtained, the nature of the vibrational modes can be determined without the necessity of carrying through the detailed dynamical treatment.⁴

34d. Method of Extreme Fields.—It is true that complete calculations will give precise information concerning the nature of the normal vibrations of a molecule, and even of the amplitudes of vibration of the nuclei, but for many purposes a general indication, such as is depicted in Fig. 27 for the YX_2 molecule, is adequate. This may be obtained by applying the *method of extreme fields*, proposed by Dennison.⁵ The general character of a normal vibration depends essentially on the symmetry properties of the molecule, as indicated in the preceding section, and not on the exact nature of the particular forces operative between the nuclei that determine the potential energy of the molecule. By postulating extreme fields, a relatively complex molecule may be regarded as effectively split up into simple units, for which the normal vibrational modes are known. The actual vibrations may then be taken as being intermediate between those that would result from the application of extreme fields.

The procedure may be explained very simply by reference to the symmetrical triangular molecule YX_2 . Suppose the forces acting between the two X atoms is very much larger than that operating between the Y atom and the X atoms; the system YX_2 may then be regarded as made up of the atom Y and the diatomic molecule X_2 . Bearing in mind that there must

⁴ Mulliken, *Phys. Rev.*, **43**, 279 (1933); Rosenthal and Murphy, *Rev. Mod. Phys.*, **8**, 317 (1936); Wilson, *Phys. Rev.*, **45**, 706 (1934); *J. Chem. Phys.*, **2**, 432 (1934); **7**, 1047 (1939); **9**, 76 (1941); Howard and Wilson, *ibid.*, **2**, 630 (1934).

⁵ Dennison, *Rev. Mod. Phys.*, **3**, 280 (1931).

be no change in the linear and angular momenta of the molecule as a whole, that is to say, the molecule must not rotate or move bodily through space, as a result of the vibrational motion, it is evident that three vibrations, of the type shown in Fig. 28, I, will be possible. In the first case (ν_1) the system X_2 , acting as a rigid bar, and the atom Y vibrate relative to one another; in the second type of vibration (ν_2) the atom Y is stationary and the two X atoms vibrate with respect to each other; and in the third case

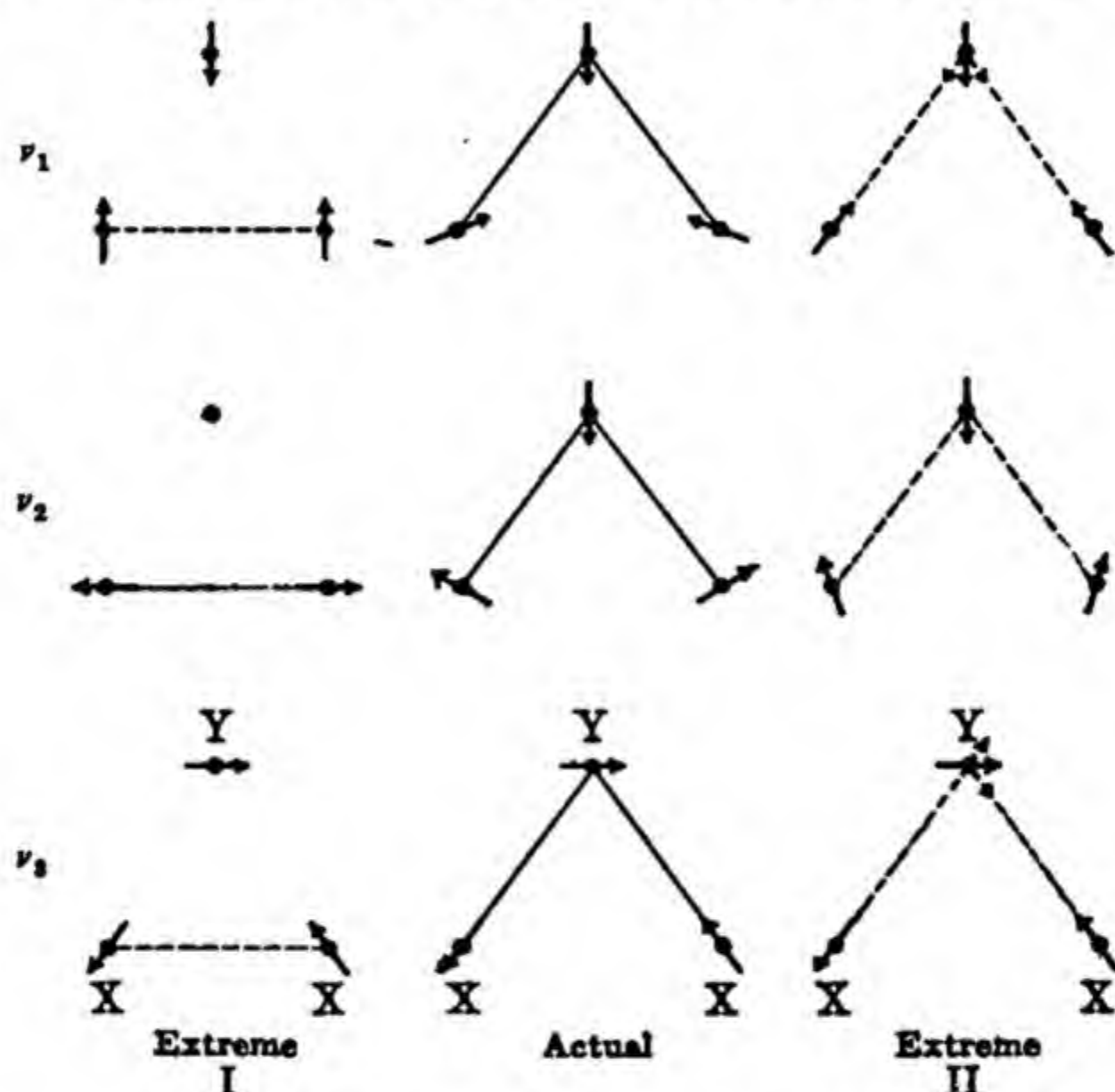


FIG. 28. Method of extreme fields

(ν_3) the X_2 again behaves as a bar, undergoing a rocking or tipping motion about its center of gravity, while the atom Y vibrates at right angles to the axis of symmetry and in the plane of the molecule.

The other type of extreme field would be that in which the Y atom was strongly bound to each of the X atoms, while the X atoms were weakly attracted to one another. The system is then virtually one consisting of two XY molecules. The three resulting vibrations are shown in Fig. 28, II. In the first case the X and Y atoms of each XY vibrate toward each other, giving the resultant shown; in the second case the two XY's rock about their centers of gravity, while in the third type of vibration each X atom oscillates relative to the Y atom in such a way that one of the former moves toward the latter while the other is moving away, and vice versa. The actual vibrational modes shown in the center of Fig. 28 represent states intermediate between the two extremes; the results are seen to be identical with the normal vibrations depicted in Fig. 27.

34e. Classification of Normal Vibrations.—Various methods of classifying the normal vibrational modes have been proposed; these are useful for

a number of purposes. One method of classification for molecules possessing an axis of symmetry depends on the direction of change of the electric dipole moment of the molecule that accompanies the vibration. This classification is important because it will be evident from what has been said in Section 27d that the results provide information on whether the particular frequency will be active or inactive in the infra-red (vibration) spectrum of the molecule. If there is no change in the dipole moment accompanying the vibration, then that particular vibration will be inactive in the infra-red spectrum. On the other hand, if the dipole moment does alter, the change may be in directions parallel or perpendicular to the symmetry axis; in the former case the vibration is said to be *parallel*, and in the latter event it is referred to as a *perpendicular* vibration. Both perpendicular and parallel vibrations will be active in the infra-red, but it will be seen later that the fine (rotational) structure of the vibration bands is characteristic of each type of vibration. This fact is of great value in the identification of the bands in the infra-red spectra with the various vibrational modes. In the case of the symmetrical angular YX_2 molecule, already considered, it is evident that all three vibrations are accompanied by changes in the electric dipole moment of the molecule. The vibrations associated with the frequencies ν_1 and ν_2 change the moment in a direction parallel to the axis of symmetry, which in this case is the line bisecting the XYX angle; these are consequently parallel vibrations, and the corresponding infra-red bands will have similar structures. The third vibration frequency ν_3 , however, results in an alteration of the dipole moment in a direction perpendicular to the symmetry axis, and hence this is called a perpendicular vibration. The question of whether a particular vibration is perpendicular or parallel is obviously determined by the symmetry characteristics of the vibration; it will thus be apparent that the necessary information, in difficult cases, can be obtained by the methods of group theory.

For the purpose of identifying various types of normal vibrations, Mecke (1930) has suggested classifying them as *valence* (stretching) vibrations, for which the symbol ν is employed, and *deformation* (bending) vibrations, indicated by the symbol δ . Of the $3n - 6$ vibrational modes of a molecule containing n atoms, $n - 1$ are valence vibrations and $2n - 5$ are deformation vibrations. It should be mentioned that this classification depends on the assumption of the so-called *valence force field*, to which reference will be made later (Section 38c). The ν vibrations essentially involve motions in the direction of the valence bonds, whereas those of the δ type are accompanied by movements at right angles to these bonds. The parallel or perpendicular nature of the vibrations can be indicated by the use of the symbols π and σ , respectively,⁶ so that $\nu(\pi)$ would represent a parallel valence vibration, $\delta(\sigma)$ would be a perpendicular deformation vibration, and so on. Referring again to the YX_2 molecule, the motion of the X atoms in the vibrations of frequencies ν_1 and ν_2 are in the direction of the X—Y bonds, and hence these are regarded as valence vibrations; the former is parallel and

⁶ From the German words *parallel* and *senkrecht*, respectively.

the latter perpendicular, so that these are $\nu(\pi)$ and $\nu(\sigma)$, respectively. In the ν_2 vibration the X atoms vibrate at right angles to the X—Y bonds, and the general form of the vibration is seen to consist of a bending of the molecule as a whole; this is to be regarded as a deformation vibration, and since it has already been shown to be parallel, it may be symbolized by $\delta(\pi)$. The results of the conventional and Mecke notations for the XY_2 molecules may be summarized in the manner indicated below.

ANGULAR YX_2 MOLECULE

Conventional symbol	ν_1	ν_2	ν_3
Mecke symbol	$\nu(\pi)$	$\delta(\pi)$	$\nu(\sigma)$

An additional, or alternative, classification of normal vibrations is sometimes convenient when the molecule possesses a center of symmetry. If the vibration does not alter any of the symmetry properties of the molecule, it is said to be a *symmetric vibration*; on the other hand, if the vibration is such that reflection of the molecule in any plane of symmetry results in a change of sign of the displacement, it is referred to as an *antisymmetric vibration*. Sometimes a normal vibration is antisymmetric with respect to one symmetry operation, and perhaps symmetric with respect to all others; nevertheless it is still called an antisymmetric vibration. For a completely symmetric vibration there must be no change with respect to all the elements of symmetry of the system. If a molecule possesses a center of symmetry its dipole moment will be zero, and since a symmetric vibration does not produce any change in the dipole moment, it follows that for such molecules symmetric vibrations will be inactive in the infra-red spectrum.

A scheme for classifying normal vibrations by utilizing the results of group theory is of particular value for relatively complex molecules when the foregoing schemes are of little practical use. The letters *A* and *B* are employed to represent nondegenerate vibrations; those in class *A* are symmetric, i.e., their sign is unchanged, for rotation by $2\pi/n$ about the principal *n*-fold axis, while those in class *B* are antisymmetric for this operation. A numerical subscript gives the value of *n* in each case, e.g., A_1 , A_2 , B_1 , B_2 , B_3 , etc. Two-fold degenerate vibrations are indicated by the letter *E*, while for three-fold degeneracy, the symbol *F* is employed. If the molecule has a center of symmetry, the letters *g* and *u* are used as subscripts to indicate that the vibrations are symmetric and antisymmetric, respectively, with respect to inversion at the center of symmetry. In some cases a single prime (') is employed to indicate that the vibration is symmetric upon reflection in a plane perpendicular to the principal axis; a double prime (") refers to a vibration that is antisymmetric for this operation.

34f. Vibrational Raman Spectra.—It was seen in Section 33c that the vibrational Raman effect is observed only when the polarizability of the molecule changes in the course of a vibration; this criterion can be applied without difficulty to simple types of normal vibrations. For the sym

metrical linear YX_2 molecule, it can be seen that the symmetric ν_1 (Fig. 29) vibration is accompanied by a change in the dimensions of the polarizability ellipsoid, and hence this frequency will be present in the Raman spectrum. On the other hand, with the normal vibrations represented by ν_2 and ν_3 , the polarization ellipsoid is unaffected, and hence these frequencies are not observed in the Raman effect. It is of interest to note that with the linear YX_2 molecule, those vibrations that are inactive in the Raman effect are active in the infra-red spectrum, and vice versa. The vibration ν_1 is not accompanied by any change in the zero dipole moment of the symmetrical molecule, but in the vibrations ν_2 and ν_3 the molecule develops an electric moment. In the case of ν_2 , for example, the molecule acquires an angular configuration in the course of the vibration, while in ν_3 the particular symmetry of the molecule, which is responsible for the zero moment, is destroyed. Attention may be called to the fact that the vibration ν_2 is doubly degenerate, for there are two identical normal vibrations, having the same frequency, in two planes at right angles to each other.

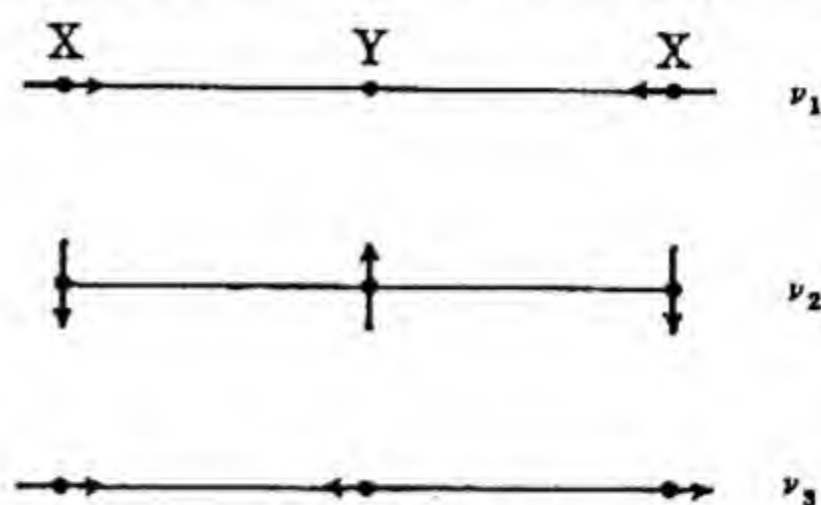


FIG. 29. Vibrations of symmetrical linear YX_2 molecule

An unsymmetrical linear triatomic molecule, XYZ , has a permanent dipole moment, and hence the three vibrations corresponding to ν_1 , ν_2 and ν_3 in Fig. 29 will all be active in the infra-red. Further, the three vibrations are accompanied by changes in the dimensions of the polarizability ellipsoid, and so they are all active in the Raman effect. Similar conclusions, that all three vibrations are active in both infra-red and Raman spectra, may be drawn from a consideration of the angular YX_2 molecule (Fig. 27).

An important property of Raman lines is that known as the *depolarization factor*, for it has been found useful in the characterization of the vibrational modes. The light scattered in the Raman effect is polarized to different extents in different directions, and the ratio of the intensity of the light polarized in a direction parallel to the incident radiation, to that polarized in a direction perpendicular to it, is called the depolarization factor, ρ . It has been shown theoretically that if the incident light is unpolarized, the maximum value of ρ is $\frac{8}{13}$, i.e., 0.86, and its minimum value is zero. In the former case the scattered radiation is said to be *completely depolarized*, while in the latter it is *perfectly polarized*; for values of ρ lying between zero and 0.86, the Raman lines are said to be *polarized*. When a normal vibration produces merely a rocking or twisting motion in the polarization ellipsoid, the corresponding Raman lines will be depolarized. It appears that, in general, vibrations that are antisymmetric with respect to one or more of the symmetry elements of the molecule give rise to Raman lines that are strongly depolarized. Rotational lines are always completely depolarized. On the other hand, if the polarization ellipsoid undergoes a periodic deformation or pulsation for a particular normal vibration, the corresponding Raman

lines will be polarized. Completely symmetrical vibrations invariably produce depolarized lines. Polarized lines are usually sharp and intense, while depolarized lines are diffuse and of low intensity. In the triangular YX_2 molecule, for example, the frequencies ν_1 and ν_2 (Fig. 27) are polarized and the corresponding Raman lines are strong; the third frequency ν_3 gives rise to a relatively weak, depolarized line. It will be noted, incidentally, in agreement with expectation, that the ν_3 frequency is completely unsymmetrical. The polarization properties of the Raman lines are thus seen to provide useful information concerning the particular vibrations responsible for those lines.

34g. Review of Normal Vibrations.—The normal modes of vibration of some simple molecules are depicted on pages 217 and 218; a dotted circle means that the motion is isotropic, i.e., not restricted to one direction, in the plane of the circle. The activity or inactivity of the various vibrations in the infra-red and Raman spectra, together with various characteristics of the vibrations are indicated in each case. It will be recalled that the letters *A* and *B* refer to nondegenerate vibrations, while *E* and *F* are used for doubly and triply degenerate vibrations. The letters *p* and *d* refer to polarized and depolarized Raman lines, respectively.

VIBRATION-ROTATION SPECTRA⁷

35a. Rotational Structure.—The most important spectra of polyatomic molecules are those appearing in the near infra-red region of the spectrum, and hence these merit treatment in some detail. As already seen, the electronic spectra are generally too complicated to be of great value, and the pure rotation spectra in the far infra-red are of limited usefulness because of experimental difficulties. Just as with diatomic molecules, the rotational changes that accompany vibrational transitions give rise to the fine structure of the vibration bands. Because of the possibility that a polyatomic molecule may have three different moments of inertia, the rotational structure is liable to be complicated. Further, since the values of these moments of inertia may be high, for relatively large molecules, the spacing between successive rotational lines is often so small that complete resolution is not possible. Nevertheless, useful information can be obtained, as will be explained shortly, from the general appearance of the band. In spite of its complexity, therefore, the study of the rotational structure of the vibration bands of polyatomic molecules is important, for it facilitates the often difficult task of correlating the observed bands with the normal vibrational modes of the molecule. The consideration of the influence of rotation on the vibration spectrum is most conveniently pursued by classifying molecules into four groups in accordance with certain relationships of the moments of inertia. In the first group are the linear molecules; these have two equal moments of inertia while the third is zero, and so they behave like diatomic molecules. The second and third groups consist of molecules having either

⁷ Dennison, ref. 5; *Rev. Mod. Phys.*, 12, 175 (1940).

XYZ linear:

Symbol	ν_1	$\nu_2(2)$	ν_3
Class	A_1	E_1	A_1
Infra-Red	ac. (π)	ac. (σ)	ac. (π)
Raman	ac. (p)	ac. (d)	ac. (p)

YX₂ linear:

Symbol	ν_1	$\nu_2(2)$	ν_3
Class	A_g	E_u	A_u
I. R.	inac.	ac. (σ)	ac. (π)
Raman	ac. (p)	inac.	inac.

XYZ angular:

Symbol	ν_1	ν_2	ν_3
Class	A'	A'	A'
I. R.	ac. (π)	ac. (π)	ac. (σ)
Raman	ac. (p)	ac. (p)	ac. (p)

YX₂ angular:

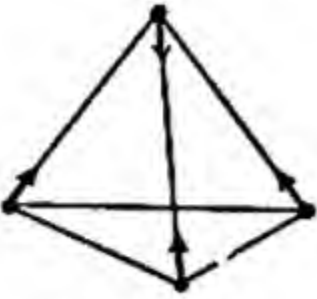


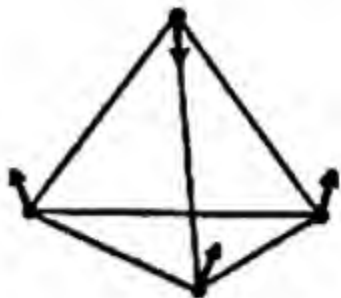
Symbol	ν_1	ν_2	ν_3
Class	A_1	A_1	B_1
I. R.	ac. (π)	ac. (π)	ac. (σ)
Raman	ac. (p)	ac. (p)	ac. (d)

X₂Y₂ linear:

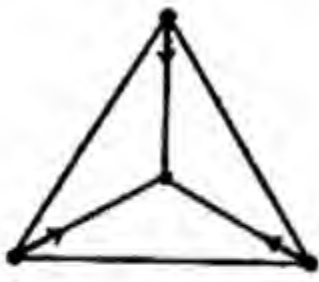
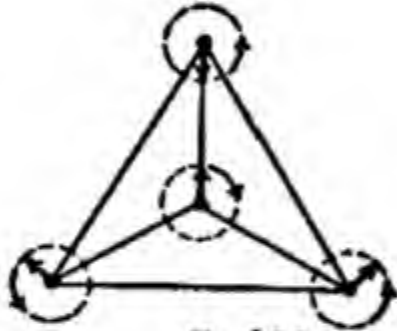
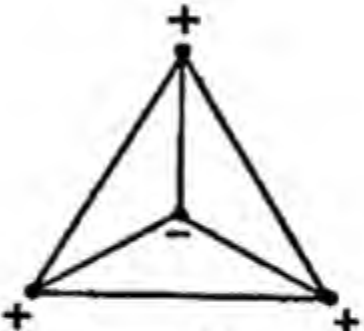
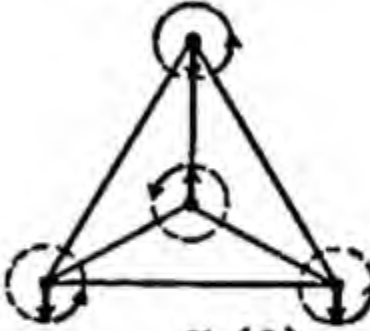
Symbol	ν_1	ν_2	$\nu_3(2)$	ν_4	$\nu_5(2)$
Class	A_{1g}	A_{1g}	E_{1u}	A'_{1u}	E_{1g}
I. R.	inac.	inac.	ac. (σ)	ac. (π)	inac.
Raman	ac. (p)	ac. (p)	inac.	inac.	ac. (d)

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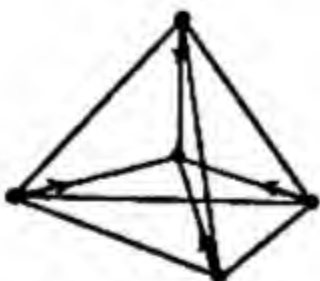
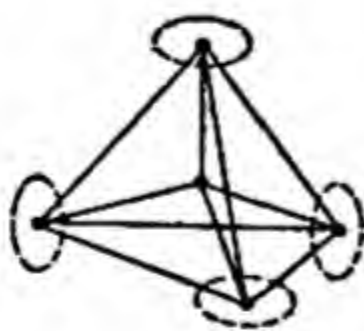
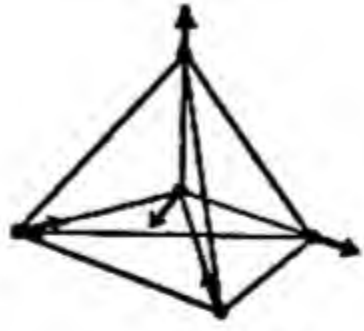
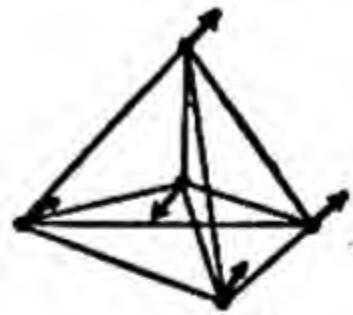
YX_3 pyramidal:

			
Symbol ν_1	$\nu_{2,4}$	$\nu_{3,5}$	ν_6
Class A_1	E	E	A_1
I. R. <i>ac.</i> (π)	<i>ac.</i> (σ)	<i>ac.</i> (σ)	<i>ac.</i> (π)
Raman <i>ac.</i> (ρ)	<i>ac.</i> (d)	<i>ac.</i> (d)	<i>ac.</i> (ρ)

YX_3 planar:

			
Symbol ν_1	$\nu_2(2)$	ν_3	$\nu_4(2)$
Class A'_1	E'	A''_2	E'
I. R. <i>inac.</i>	<i>ac.</i> (σ)	<i>ac.</i> (π)	<i>ac.</i> (σ)
Raman <i>ac.</i> (ρ)	<i>ac.</i> (d)	<i>inac.</i>	<i>ac.</i> (d)

YX_4 tetrahedral:

			
Symbol ν_1	$\nu_2(2)$	$\nu_3(3)$	$\nu_4(3)$
Class A_1	E	E_1	F_2
I. R. <i>inac.</i>	<i>inac.</i>	<i>ac.</i>	<i>ac.</i>
Raman <i>ac.</i> (ρ)	<i>ac.</i> (d)	<i>ac.</i> (d)	<i>ac.</i> (d)

two equal moments of inertia and the third different from zero (symmetrical top molecules), or those with all three moments of inertia equal (spherical molecules). In the fourth group are the asymmetrical top molecules which have three different moments of inertia.

35b. Linear Molecules.—The expression for the energy of a linear rotator is identical with that already given in Section 28a for a diatomic molecule, viz.,

$$E_r = \frac{h^2}{8\pi^2 I} J(J + 1), \quad (35.1)$$

where, as before, J is the rotational quantum number, which may be zero or integral, and I is the moment of inertia of the molecule. As indicated above, a linear molecule really has two moments of inertia that differ from zero, but they are identical; it is justifiable, therefore, to refer to the one moment of inertia of the molecule. The vibrational energy for a particular normal vibration of frequency ν cm.⁻¹ may be represented by the general equation

$$E_v = (v + a)h\nu, \quad (35.2)$$

where the vibrational quantum number v may be zero or an integer; a is equal to $\frac{1}{2}$ for a linear oscillator, but it is unity for a two-dimensional oscillator, e.g., the ν_2 vibration of the linear YX_2 molecule (Fig. 29). If, as a first approximation, the rotational and vibrational energies are taken as being strictly additive, then

$$E_{vr} = (v + a)h\nu + \frac{h^2}{8\pi^2 I} J(J + 1). \quad (35.3)$$

In order to derive an expression for the frequency of the spectral lines resulting from vibration-rotation transitions, it is necessary to have some information concerning the selection rules applicable to this particular case. As far as the vibrational transition is concerned, the rule that has been given previously for diatomic molecules is applicable, namely $\Delta v = 1$. The selection rules for the rotational transitions associated with a particular vibrational change depend on whether the vibrational mode is of the parallel or perpendicular type (Section 34e). It will be convenient therefore to consider these two cases separately.

Parallel Bands: The selection rule for a rotational change associated with a parallel vibration of a linear molecule has been shown by the methods of quantum mechanics to be the same as for a normal diatomic molecule, viz., $\Delta J = \pm 1$. If the rotational transition is $J \rightarrow J - 1$, so that ΔJ is -1 , then the fine structure lines of the *negative* or *P branch* of the vibration-rotation band are obtained; thus, taking Δv as $+1$ and ΔJ as -1 , it follows from equation (35.3), by the method used in Section 29c, that

$$J \rightarrow J - 1: \quad \nu(P) = \nu_r - \frac{h}{4\pi^2 I_c} J, \quad (35.4)$$

the suffix π being introduced into ν_π to show that this equation refers to parallel vibrations. Similarly, for the *positive* or *R branch*, when ΔJ is $+1$, it is found that

$$J - 1 \rightarrow J: \quad \nu(R) = \nu_\pi + \frac{h}{4\pi^2 I_c} J. \quad (35.5)$$

The rotational structure of the infra-red band for a parallel vibration of a linear polyatomic molecule, will thus be of exactly the same type as for a diatomic molecule. The frequency separation between successive lines in either the *P* or the *R* branch is $h/4\pi^2 I_c$; the central line (*Q* branch), for which ΔJ is zero, is missing, as with a diatomic molecule, and so the spacing of the gap at the center of the band will be $h/2\pi^2 I_c$. The foregoing results are, of course, based on the assumption that the molecule is a rigid rotator. In actual fact the molecule will not be rigid, and so the spacings will be somewhat different from those just derived (cf. Section 29e).

Perpendicular Bands: With a perpendicular type of vibration, it is permissible for a transition to occur for which ΔJ is zero, as well as ± 1 . This means that a *Q* branch is possible, in addition to the *P* and *R* branches. According to equation (35.1), the frequencies of the lines in the various bands are given by

$$J \rightarrow J - 1: \quad \nu(P) = \nu_\pi - \frac{h}{4\pi^2 I_c} J \quad (35.6)$$

$$J \rightarrow J: \quad \nu(Q) = \nu_\pi \quad (35.7)$$

$$J - 1 \rightarrow J: \quad \nu(R) = \nu_\pi + \frac{h}{4\pi^2 I_c} J. \quad (35.8)$$

It would appear, at first sight, that the *Q* branch consists of a single line; however, owing to the interaction of the energies of vibration and rotation, it is actually a relatively broad diffuse band.

It is the presence of a fairly intense *Q* branch in the center of a perpendicular vibration band that distinguishes it clearly from parallel bands of a linear polyatomic molecule. As far as other characteristics are concerned, the two types of bands are very similar; the separation of successive lines in both *P* and *R* branches should be equal to $h/4\pi^2 I_c$, apart from nonrigidity corrections, in each case.

35c. Symmetrical Top Molecules.—A symmetrical top molecule has two moments of inertia (A and B) that are equal, while the third (C) is different; examples of this type are the pyramidal YX_3 molecules, such as NH_3 , PCl_3 , etc., and the tetrahedral ZYX_3 molecules, such as $CHCl_3$, CH_3Cl , etc. The rotational energy for a symmetrical top molecule is found by wave mechanics to be given by the equation

$$E_r = \frac{h^2}{8\pi^2 A} J(J + 1) + \frac{h^2}{8\pi^2} \left(\frac{1}{C} - \frac{1}{A} \right) K^2, \quad (35.9)$$

where J is the quantum number for the total angular momentum of the molecule, and K is the quantum number for the angular momentum about the symmetry axis (cf. Section 30e). By convention, C is taken as the moment of inertia of the molecule about its symmetry axis, while A is the other moment of inertia. The possible values of J are $0, 1, 2, \dots$, whereas K may be $0, \pm 1, \pm 2, \dots, \pm J$, that is, $J \geq |K|$; there are thus $2J + 1$ values of K for each J value. If the energies of vibration and rotation are assumed to be additive, the total vibrational-rotational energy may be obtained by adding equations (35.2) and (35.9). The frequencies of the rotation lines in the vibration band may then be derived in the usual manner if the selection rules are known; as in the previous case, Δv is 1, but the values of ΔJ and ΔK depend on whether the vibration is of the parallel or perpendicular type.

Parallel Bands: For a parallel vibration of a symmetrical top molecule, ΔJ is zero or ± 1 , while ΔK is zero. It is evident that P , Q and R branches will be found in the vibration band, the frequencies of the respective lines being given by

$$J \rightarrow J - 1: \quad \nu(P) = \nu_r - \frac{h}{4\pi^2 A_c} J \quad (35.10)$$

$$J \rightarrow J: \quad \nu(Q) = \nu_r \quad (35.11)$$

$$J - 1 \rightarrow J: \quad \nu(R) = \nu_r + \frac{h}{4\pi^2 A_c} J. \quad (35.12)$$

These are seen to be analogous to equations (35.6), (35.7) and (35.8) for the frequencies of the corresponding bands in the perpendicular vibrations of a linear molecule. As in other cases, the Q branch is actually a fairly broad diffuse band, instead of a single line, because of interaction between the rotational and vibrational energies. It will be immediately apparent that the rotational structure of a parallel band of a symmetrical top molecule will be very similar to that of a perpendicular band of a linear molecule. The separation of the rotational lines in the P and R branches is equal to $h/4\pi^2 A_c$, where A is the moment of inertia of the molecule about an axis perpendicular to the symmetry axis; there are, of course, two such directions, but for a symmetrical top molecule the moments about these directions are the same, as noted above.

Perpendicular Bands: In the case of a perpendicular vibration of a symmetrical top molecule, the selection rules permit a change of ± 1 in the quantum number K , simultaneously with changes in J ; thus, the allowed rotational transitions are $\Delta J = 0, \pm 1$, and $\Delta K = \pm 1$. For each change in K there will thus be a band with P , Q and R branches, and the complete perpendicular vibration band, for $\Delta v = 1$, will be made up by the superposition of a number of separate bands, each corresponding to a permitted change in the value of K . If ΔK is -1 , e.g., the transition is $K \rightarrow K - 1$,

then the frequencies of the various lines are given by

$$\left. \begin{array}{l} J \rightarrow J - 1 \\ K \rightarrow K - 1 \end{array} \right\} \quad \nu(P) = \nu_0 - \frac{h}{4\pi^2 A c} \{J + \beta(K - \tfrac{1}{2})\},$$

$$J = K, K + 1, \dots \quad (35.13)$$

$$\left. \begin{array}{l} J \rightarrow J \\ K \rightarrow K - 1 \end{array} \right\} \quad \nu(Q) = \nu_0 - \frac{h}{4\pi^2 A c} \beta(K - \tfrac{1}{2}) \quad (35.14)$$

$$\left. \begin{array}{l} J - 1 \rightarrow J \\ K \rightarrow K - 1 \end{array} \right\} \quad \nu(R) = \nu_0 + \frac{h}{4\pi^2 A c} \{J - \beta(K - \tfrac{1}{2})\},$$

$$J = K + 1, K + 2, \dots \quad (35.15)$$

where β is determined by the two moments of inertia, and is defined by

$$\beta = \frac{A}{C} - 1. \quad (35.16)$$

For each value of K these equations represent a vibration-rotation band similar to that for a parallel vibration, as given by equations (35.10), (35.11) and (35.12); it will be noted, however, that for the perpendicular vibration the rotation lines are displaced bodily to the low frequency side by an amount $\beta(K - \frac{1}{2})h/4\pi^2 A c$. As K increases, therefore, the center of the band, represented by the position of the Q branch, moves towards regions of lower frequency. There is a somewhat unusual feature of the perpendicular bands for a symmetrical top to which attention may be called. It will be seen from an examination of the possible J values that the first line to appear in the P branch will be the one having a J value equal to K , whereas for the first line of the R branch, J will be equal to $K + 1$. It follows, therefore, that the first K lines of the P branch and the first $K + 1$ lines of the R branch at the center of the band will be missing. Thus when K is 1, none of the P lines will be absent, but the first R line will be missing; for $K = 2$, there will be one P line and two R lines absent from the vicinity of the center of the band. In every case, however, there will be a strong Q branch in this position. It will be remembered that equations (35.13), (35.14) and (35.15), and the foregoing discussion, refer to a change of K to $K - 1$, that is, for $\Delta K = -1$; the resulting bands for the various values of K are consequently called *negative subsidiary bands*. When K is 1, the band is referred to as the first negative subsidiary band; when K is 2 it is called the second negative subsidiary band, and so on.

When the value of K increases in a vibration-rotation transition, i.e., ΔK is $+1$, there results the series of *positive subsidiary bands*. The frequencies of the lines in the P , Q and R branches are now given by the

following expressions:

$$\left. \begin{array}{l} J \rightarrow J-1 \\ K-1 \rightarrow K \end{array} \right\} \quad \nu(P) = \nu_0 - \frac{h}{4\pi^2 A c} \{J - \beta(K - \tfrac{1}{2})\},$$

$$J = K+1, K+2, \dots \quad (35.17)$$

$$\left. \begin{array}{l} J \rightarrow J \\ K-1 \rightarrow K \end{array} \right\} \quad \nu(Q) = \nu_0 + \frac{h}{4\pi^2 A c} \beta(K - \tfrac{1}{2}) \quad (35.18)$$

$$\left. \begin{array}{l} J-1 \rightarrow J \\ K-1 \rightarrow K \end{array} \right\} \quad \nu(R) = \nu_0 + \frac{h}{4\pi^2 A c} \{J + \beta(K - \tfrac{1}{2})\},$$

$$J = K, K+1, \dots \quad (35.19)$$

equations represent a series of bands similar to those belonging to the series; their centers are now, however, displaced to the high frequency side to the extent of $\beta(K - \frac{1}{2})h/4\pi^2 A c$. As before, each subsidiary band has a strong Q branch at the center, but the first $K+1$ lines in the P branch and the first K lines in the R branch are missing from each band.

In any subsidiary band, positive or negative, that is, for a given K value, the separation between successive rotational lines, except in the center of the band where some lines may be absent, is equal to $h/4\pi^2 A c$. This result is readily obtained from a consideration of the various equations giving the frequencies of the lines in the P and R branches. From the expressions for frequencies of the Q branches, on the other hand, it is seen that the frequency separation between the Q branches of any two successive subsidiary bands should be $\beta h/4\pi^2 A c$. In view of the definition of β , by equation 16), this separation is

$$\Delta\nu_Q = \frac{h}{4\pi^2 c} \left(\frac{1}{C} - \frac{1}{A} \right). \quad (35.20)$$

It follows, therefore, that in principle, at least, the two moments of inertia, A and C , may be determined from the frequency separation of the rotational lines, which gives A , and from the separation of the Q branches from which, knowing A , the value of C may be derived. In practice the rotational lines of the perpendicular bands are so close, largely because of the partial superposition of the various subsidiary bands, that there is little possibility of evaluating A in this manner. However, the parallel bands of the same molecule are relatively simple, as shown by equations (35.10) and (35.12), and the moment of inertia A can most readily be obtained from the separation of successive rotational lines in the P and R branches of these bands; as seen above, this frequency separation is also $h/4\pi^2 A c$. If A is made available in this manner, C can then be obtained by means of equation (35.20) from the frequency separation between successive Q branches in the perpendicular bands. A difficulty often arises in this connection, however, because the P and R branches of the several superimposed subsidiary bands may be

so strong as to obscure the Q branches, in spite of the relatively high intensity of the latter.

Even when the positions of the Q branches can be identified in the perpendicular bands, it is sometimes found that the spacing varies markedly from one subsidiary band to another. This result is, of course, contrary to the theory given above, and the anomalous behavior is most probably due to interaction between rotational and vibrational motions. It has been suggested that as a result of the rotation of the symmetrical top molecule about its symmetry axis, a force is developed in the perpendicular vibrations which gives rise to an additional (internal) angular momentum. This naturally affects the rotational energy of the molecule, and consequently the separation of the Q branches. Instead of the normal spacing between Q branches, given by equation (35.20), it appears that the actual frequency separation should be represented by

$$\Delta\nu_Q = \frac{h}{4\pi^2c} \left(\frac{1-\xi}{C} - \frac{1}{A} \right), \quad (35.21)$$

where ξ gives the number of $h/2\pi$ units of internal angular momentum resulting from the interaction just described. If there were no such interaction, ξ would be zero and equation (35.21) would reduce to (35.20). The value of ξ is different for different perpendicular bands—hence the difference in the Q branch spacings—and is a complicated function of the masses of the atoms and of the force constants involved in the expression for the potential energy of the molecule. There are, however, certain relatively simple *sum rules*, which are independent of the potential function, but are determined by the form of the molecule only. If $\sum\Delta\nu_Q$ represents the sum of the mean Q branch spacings in the perpendicular bands of a particular symmetrical top molecule, then if the latter is of the pyramidal YX_3 type, which has two perpendicular bands,

$$\sum\Delta\nu_Q = \frac{h}{4\pi^2c} \left(\frac{3}{C} - \frac{5}{2A} \right),$$

while if it is of the tetrahedral ZYX_3 type, with three perpendicular bands,

$$\sum\Delta\nu_Q = \frac{h}{4\pi^2c} \left(\frac{3}{C} - \frac{7}{2A} \right).$$

It is seen, therefore, that if the moment of inertia A is determined from the separation of the rotational lines in a parallel band, it is possible to evaluate the other moment of inertia C , provided the Q branch spacings in all the perpendicular bands of the molecule are known.

35d. Band Envelopes of Symmetrical Top Molecules.—Because of the complexity of the perpendicular bands of many polyatomic molecules, it is not practicable, with the means at present available, to resolve the separate rotational lines. It is possible, nevertheless, to obtain some useful informa-

tion from the external contour (or envelope) of the complete band. In the previous section the general principles upon which a perpendicular band is constructed have been developed; if, in addition, something were known concerning the relative intensities of the various lines, it should be possible to derive from theory the general shape of the *envelope* of the band. (The envelope is the curve representing the variation of intensity throughout a band as a function of the frequency, the fine structure being ignored.) Expressions have been derived, from quantum theory and the Maxwell-Boltzmann distribution law, which give the intensities of rotational lines as a summation involving the rotational quantum numbers, the moments of inertia, and other factors. By assuming that the moment of inertia A is not too small, the summation may be replaced by integration, and the intensities can then be calculated. Working in this manner, the shapes of the envelopes for a series of values of the moment of inertia factor β have been derived. These envelopes were found to vary considerably with the magnitude of β ; hence the shape of the envelope can be used both to identify a perpendicular band, since a parallel band gives an entirely different type of envelope, and to give some indication of the value of β . Since the latter depends on the ratio of the moments of inertia, it will provide helpful information concerning the shape of the molecule.

35e. Spherical Molecules.—The rotational structure of the vibrational bands of a spherically symmetrical molecule, such as CH_4 and CCl_4 , is relatively simple, at least in principle. The three moments of inertia of such a molecule are equal ($A = B = C$), and in this case, since $C = A$, it is evident from equation (35.9) that the rotational energy is given by an equation similar in form for that of a diatomic molecule, viz.,

$$E_r = \frac{h^2}{8\pi^2 A} J(J + 1).$$

The only vibrations that are active in the infra-red are those that are anti-symmetric with respect to the center of symmetry of the molecule, and for these the selection rule for rotational transitions is $\Delta J = 0, \pm 1$. Since Δv is, as before, limited to unity, the vibration bands should consist of simple P , Q and R branches; the equations giving the frequencies of the rotational lines will be

$$J \rightarrow J + 1: \quad \nu(P) = \nu - \frac{h}{4\pi^2 A c} J \quad (35.22)$$

$$J \rightarrow J: \quad \nu(Q) = \nu \quad (35.23)$$

$$J - 1 \rightarrow J: \quad \nu(R) = \nu + \frac{h}{4\pi^2 A c} J. \quad (35.24)$$

According to these equations, not only should the Q branch consist of a single line, but the separation of successive rotational lines in the P and R branches should be constant, and equal to $h/4\pi^2 A c$, in all the bands. Ac-

tually, as may be anticipated, neither of these expectations is fulfilled in practice: the Q branches consist of a number of closely spaced lines, and the rotational separations in the P and R branches vary from one band to another. One reason for this is, of course, the nonrigidity of the molecule, but another reason for the lack of constancy in the separation of successive lines in different bands is the type of interaction between rotation and vibration described above for symmetrical top molecules. If $\Delta\nu$ now represents the frequency separation of the rotational lines, then

$$\Delta\nu = (1 - \xi) \frac{h}{4\pi^2 Ac},$$

where, as before, ξ is the quantum number for the internal angular momentum resulting from the interaction. Again ξ is a complicated quantity, but the sum of the rotational spacings for the two infra-red bands of a spherical molecule, which is given by

$$\sum \Delta\nu = \frac{3h}{8\pi^2 Ac},$$

does not involve ξ . It is thus possible to calculate the moment of inertia A if the rotational separations in the two infra-red active bands are measured. It should be mentioned, incidentally, that the spacing of the rotational lines in the fundamental vibration bands of symmetrical molecules provides a clue to the association of these bands with particular normal vibrational modes.

35f. Asymmetrical Top Molecules.—When the three moments of inertia of a molecule about axes at right angles are all different, the molecule is referred to as an asymmetrical top. As is to be expected, the rotational fine structure of the vibration bands of such molecules is very complicated. The complexity arises because of a situation that is somewhat analogous to that occurring in the perpendicular bands of symmetrical top molecules. The angular momentum of the molecule, and hence the rotational energy, is determined by two quantum numbers J and K , there being, as before $2J + 1$ values of K for each J value. Although the rotational transitions are restricted to $\Delta J = 0, \pm 1$, there are many possibilities for changes in K which lead to a multiplicity of rotational lines. For example, in the case of an asymmetrical top whose electrical dipole moment lies parallel to the direction of the axis with the middle moment of inertia, there should be sixteen lines for the rotational transition $J = 3$ to $J = 4$. This may be compared with the corresponding seven lines for the perpendicular band of a symmetrical top molecule. With increasing values of J , the number of rotational lines in the vibration band of an asymmetrical top molecule increases rapidly, and so the vibration-rotation spectrum becomes very complex.

Although there is no simple expression for the energies of the rotational levels, it is nevertheless possible, as a result of lengthy calculations, to evaluate these energies if the three moments of inertia of the asymmetrical top

are known. If information concerning the size and shape of the molecule were available from other sources, the moments of inertia could then be calculated and compared with those derived from the vibration bands. However, because of the large number of such lines, there are very few cases in which sufficient precise information is available for this calculation to have any value.

When the asymmetrical top molecule is planar, e.g., water and benzene, so that the sum of two of the moments of inertia is equal to the third, i.e., $A + B = C$, the vibration bands have certain characteristics which are of considerable value for identification purposes. The bands have been shown to be of three types, according as the change of the dipole moment in the course of a vibration is along the axis of the (i) smallest moment of inertia, (ii) middle moment of inertia, or (iii) largest moment of inertia.

(i) If the change of dipole moment is along the axis giving the smallest moment of inertia, the band is said to be a *type A band*. In such bands the rotational lines near the center are very closely spaced so that the *Q* branch appears to be very strong. The smaller the value of the ratio of the moments of inertia A/B , the more intense are the lines in the center of the band. As the ratio A/B approaches unity, the molecule approximates more closely to a symmetrical top with $A = B = \frac{1}{2}C$; the type *A* band under these circumstances resembles the perpendicular band of a symmetrical rotator.

(ii) For *type B bands* the change of electric moment is along the axis having the middle moment of inertia; the rotational lines in these bands are more spread out and there is a marked gap in the center, especially when the ratio of the moments of inertia A/B is small. As the ratio A/B approaches unity, the difference between type *A* and type *B* bands will, obviously, become less marked, and both resemble the perpendicular bands of symmetrical top molecules.

(iii) When the dipole moment changes in the direction of the axis having the largest moment of inertia, the resulting bands are called *type C bands*; here again the lines accumulate near the center of the band giving the appearance of a strong *Q* branch. As the moments of inertia A and B approximate to each other in value, the band takes on the appearance of the parallel type band of a symmetrical rotator.

The fine structure of the vibration bands cannot be resolved unless the moments of inertia are small, and this is only the case for such simple molecules as water and hydrogen sulfide. In other cases it is possible to obtain only the envelopes of the bands, but a knowledge of these is of value. Calculations have been made which give the general form of these envelopes for the *A*, *B* and *C* type bands of asymmetrical top molecules for various values of two parameters which are functions of the three moments of inertia. The results are not restricted to flat molecules, and are useful for identification of the fundamental bands with the various possible normal modes of vibration of the molecule.

35g. Vibration-Rotation Raman Spectra.—Very few cases of the theoretically possible rotational structure associated with vibrational Raman

lines have been observed. With improvements in technique it is possible that many Raman spectra could be resolved so as to permit the rotational lines to be studied. The selection rules differ somewhat from those which are applicable to vibration bands in the infra-red spectrum. Thus, for linear molecules, ΔJ is 0, ± 2 for parallel bands, and ± 1 , ± 2 for the perpendicular bands; a Q branch should thus be present in the former but not in the latter. For symmetrical top molecules, $\Delta K = 0$ and $\Delta J = 0, \pm 1, \pm 2$ for vibrations parallel to the symmetry axis of the molecule, whereas for vibrations perpendicular to this axis $\Delta K = \pm 1, \pm 2$ and $\Delta J = 0, \pm 1, \pm 2$. Interaction between rotations should lead to abnormal spacings in the perpendicular bands, just as with the infra-red spectra. The only type of Raman band of a spherical molecule which can exhibit a rotational structure is that due to a vibration that is not totally symmetrical. For such a band the selection rule is $\Delta J = 0, \pm 1, \pm 2$. A similar rule is applicable to the Raman bands of asymmetrical top molecules. It is evident that in view of the large number of permitted rotational transitions, the structures of Raman vibration bands of polyatomic molecules are likely to be complicated. If they could be resolved, however, they would provide information concerning the moments of inertia of the molecule which would supplement that derived from the infra-red spectra.

36a. Pure Rotation Spectra.—As in the case of diatomic molecules, the study of pure rotation spectra of polyatomic molecules in the far infra-red region is restricted by experimental difficulties. Since the moments of inertia are relatively high, the pure rotation bands of polyatomic molecules appear at very small frequencies, i.e., at very long wave lengths. Because of the complexity of vibration-rotation bands, especially when two or more bands overlap, there would be many advantages associated with the experimental study of pure rotation spectra in the far infra-red if a satisfactory technique could be developed. The work done so far has been restricted to comparatively light molecules, such as water, ammonia and phosphine; the bands for these substances are found in the nearer parts of the far infra-red region of the spectrum.

There is relatively little that can be said about the structures of the pure rotation bands; as with the vibration-rotation bands, the subject will be considered in relation to the moments of inertia of the molecule. For a linear molecule, a pure rotation band is possible only when the substance possesses a permanent dipole moment (cf. Section 27d). The rotational energy levels are given by equation (35.1), and since the selection rule is $\Delta J = \pm 1$, the frequencies of the pure rotation lines will be

$$\nu_r = \frac{h}{4\pi^2 I c} J, \quad \text{where} \quad J = 1, 2, 3, \dots \quad (36.1)$$

The frequency separation of successive lines is thus $h/4\pi^2 I c$, and the general nature of the rotation band should be the same as for a diatomic molecule. It will be observed that as the moment of inertia I increases, so the frequency

of the rotational lines, for a given J value, decreases. For relatively heavy or large molecules, the pure rotation spectrum will thus appear in the very far infra-red.

With symmetrical top molecules, it is only rotation about an axis perpendicular to the symmetry axis that can produce a changing dipole moment, and hence be active in the infra-red. The energies of the rotational levels are given by equation (35.9), and since the selection rules require that $\Delta J = \pm 1$ and $\Delta K = 0$, it is evident that the frequencies of the rotational lines will be represented by the expression

$$\nu_r = \frac{h}{4\pi^2 A c} J, \quad (36.2)$$

where A is the moment of inertia about either of the axes perpendicular to the symmetry axis. It is apparent, therefore, that the frequency separation of such lines in the pure rotation spectrum is $h/4\pi^2 A c$, and hence depends only on the moment of inertia A . The pure rotation band thus provides no information concerning the moment of inertia C , i.e., the one about the symmetry axis.

Pure rotation of a spherically symmetrical molecule, which will have no permanent dipole moment, cannot be accompanied by a changing moment, and so molecules of this type are never active in the far infra-red spectrum. Asymmetric top molecules, on the other hand, give rise to pure rotation bands of a complex character. The general considerations are similar to those discussed in Section 35f for the vibration-rotation bands; the selection rules vary according as the direction of the permanent dipole moment of the molecule lies along the axis of largest, middle or smallest moment of inertia.

36b. Pure Rotation Raman Spectra.—The pure rotation Raman spectra of a number of molecules have been studied, but their value is limited by the difficulty of resolving the rotational lines; when this resolution can be achieved, the results are of great interest because of the relative simplicity of the spectra. For linear polyatomic molecules the selection rules are identical with those for diatomic molecules, as given in Section 33e, and nothing need be added to what was stated there. Symmetrical top molecules yield Raman spectra for rotations perpendicular to the symmetry axis; the rotation about this axis produces no change in the polarizability of the molecule and hence is inactive. The rotational energy is given by equation (35.9) and the selection rule is that $\Delta J = 0, \pm 1, \pm 2$ and $\Delta K = 0$; the pure Raman rotation band will thus contain five branches, viz., O, P, Q, R and S (cf. Section 33f). Since rotation of a molecule that is spherically symmetrical cannot possibly be accompanied by any change in polarizability, these molecules give no pure rotation Raman spectrum. According to theory, the selection rule for an asymmetrical top molecule is $\Delta J = 0, \pm 1, \pm 2$; however, only those rotations that are associated with a change in the polarizability of the molecule are active in producing Raman lines. For

example, the rotation of the water molecule about its axis of symmetry will be inactive. Calculation of the frequency separations of the Raman lines for an asymmetrical top molecule are very difficult, for the same reasons as were given in Section 35f.

37. Special Effects in Vibration-Rotation Spectra.—In the discussion of the previous sections, the molecule has been assumed to behave more or less ideally, but in actual practice a number of special effects arise to which brief reference will be made.

Overtone and Combination Bands: If the oscillations of a polyatomic molecule were strictly harmonic in character, vibrational transitions would be limited to $\Delta v = 1$ for one particular mode at a time, with the Δv values for all other modes equal to zero. Because of anharmonicity, however, not only are such transitions as $\Delta v = 2, 3$, etc., permitted in certain cases, but in addition it is possible for simultaneous changes to occur in the quantum numbers of two or more vibrational modes. The former type of transition yields the overtones, and the latter gives rise to *combination bands* whose frequencies may be expressed, very approximately, by an equation of the form

$$\nu = n_1\nu_1 + n_2\nu_2 + n_3\nu_3 + \cdots, \quad (37.1)$$

where ν_1, ν_2, ν_3 , etc., represent the frequencies of the various normal modes of vibration and n_1, n_2, n_3 , etc., are small integers or zero. Correction terms for anharmonicity and interaction effects should be included in equation (37.1), but these may be disregarded here. Symmetry and other considerations limit the possibilities concerning overtone and combination bands; hence, the situation, although often complicated enough, is not as complex as it might otherwise have been. For example, if a molecule possesses a center of symmetry, totally symmetric vibrations do not give overtones, whereas for antisymmetric vibrations the first, third, etc., overtones are forbidden. Further, in the formation of combination tones, the possible values of n_1, n_2 , etc., in equation (37.1) depend on the symmetry class of the molecule and on the direction of change of the electric dipole moment for the particular vibrations.

Isotope Effects: As is the case with diatomic molecules, isotopic changes are accompanied by changes in the normal vibrations. It will be evident from Section 34a that the frequencies of these vibrations are determined largely by the masses of the atoms, which give the a_{ij} terms, and by the force constants, which are related to the b_{ij} terms. The latter are probably unaltered by an isotopic substitution, but the former must be affected; the exact nature of the change in the normal vibration frequency is evidently not expressible in such a simple form as was possible for diatomic molecules (Section 29h). Further reference to the importance of isotopes in the study of polyatomic molecules will be made in Section 38c.

*Accidental Resonance Degeneracy:*⁸ In addition to the type of degeneracy which occurs when a molecule has two vibrations with identical frequencies.

⁸ Fermi, *Z. Physik*, **71**, 250 (1931); Dennison, *Phys. Rev.*, **41**, 304 (1932).

there is another type resulting from the accidental fact that one normal vibration frequency happens to be almost exactly a simple multiple of another. For example, if the first overtone frequency of one vibrational mode, i.e., $2\nu_2$, happens to coincide with the fundamental vibration frequency of another mode, i.e., ν_1 , then if the symmetry properties of the two vibrations are the same, resonance will occur, with the result that the two modes become indistinguishable. The wave functions of the two states corresponding to the frequencies ν_1 and $2\nu_2$ are shared, and two new wave functions are obtained. The spectrum will then not correspond to that for one fundamental and one overtone, but will approximate to that expected for two fundamentals. The best known case of *accidental resonance degeneracy*, as this behavior is called, is found in the Raman spectrum of carbon dioxide. The frequency of the Raman active parallel vibration frequency (ν_1) is estimated to be 1322 cm.^{-1} ; in addition there is an inactive (infra-red active) perpendicular vibration (ν_2) of frequency 668 cm.^{-1} , so that ν_1 is approximately equal to $2\nu_2$. The Raman spectrum of carbon dioxide actually shows two strong lines at 1286 and 1388 cm.^{-1} , which cannot be accounted for satisfactorily in any other way than by postulating accidental resonance.

*Resonance due to Double Potential Minima:*⁹ Another type of resonance interaction has been brought to light by the study of the infra-red spectra of the ammonia molecule; the lines of the vibration-rotation bands for the parallel vibrations and those of the pure rotation spectrum exhibit a doublet structure. This phenomenon is attributed to the fact that the ammonia molecule, which has a pyramidal configuration with the nitrogen atom at the apex, can exist in two forms of identical energy; one in which the nitrogen is above the plane of the hydrogen atoms, and the other in which it is below this plane. The two forms are physically indistinguishable, and since they have the same energy, resonance occurs between them. In a physical sense this may be regarded as an oscillation of the nitrogen atom between two similar positions, one above and one below the plane of the hydrogen atoms. The potential energy curve for a system of this type consists of two identical parabola-like curves joined by a relatively low barrier. There are thus two identical potential minima, and hence the problem is frequently referred to as the *double-minimum problem*.

Wave mechanical calculations show that as a result of the resonance between the two levels of the same energy, one in each part of the double curve, each energy level of the molecule is split into two levels; the wave function of one is symmetric with respect to reflection in the base of the pyramid, while the other is antisymmetric for this operation. Transitions between symmetric and between antisymmetric levels are forbidden in the infra-red, and only those between a symmetric state in one level with an antisymmetric state in another are permitted. The result of the resonance is consequently a doubling of the lines in the spectrum. Similar effects have been observed in the Raman spectrum; the selection rule is, however, differ-

⁹ Dennison and Uhlenbeck, *Phys. Rev.*, **41**, 313 (1932); Manning, *J. Chem. Phys.*, **3**, 36 (1935); Wall and Glocker, *ibid.*, **5**, 314 (1937).

ent in this case. Transitions between similar states only are permitted, whereas those between symmetric and antisymmetric levels are prohibited.

By making certain assumptions concerning the shape of the double-minimum potential energy curve, it is possible to calculate the height of the pyramid, i.e., the vertical distance between the nitrogen atom and the plane of the hydrogen atoms in the ammonia molecule, from the observed frequency separation of the rotation doublets. This frequency separation should decrease rapidly with increasing height of the pyramid, and it is of interest to note that the doublet separation has not been observed in the rotation-vibration or other bands of phosphine and arsine. These molecules are evidently much taller pyramids than is the ammonia molecule, and this conclusion is supported by the bond angles which are largest in the latter case.

Nuclear Spin Effects: Symmetrical linear polyatomic molecules exhibit alternating intensities of rotational lines, just as do diatomic molecules. For a triatomic linear molecule YX_2 , the relative intensities of the lines are determined by the spins of the X nuclei; in other words, it behaves in this respect like an X_2 molecule. If the X nucleus has a spin quantum number of zero, e.g., oxygen, alternate rotational lines will be missing; this is the case for carbon dioxide, which is a linear symmetrical molecule. If the linear molecule contains two pairs of identical atoms, e.g., acetylene, with nuclear spins i_1 and i_2 , the ratio of the intensities of alternate lines is equal to $(2i_1i_2 + i_1 + i_2 + 1)/(2i_1i_2 + i_1 + i_2)$. In acetylene, the spin of the carbon atom (i_1) is zero, while that of the hydrogen atom (i_2) is $\frac{1}{2}$, so that the ratio of the intensities is 3 to 1, as in the case of the hydrogen molecule.

APPLICATIONS OF MOLECULAR SPECTRA

38a. Assignment of Frequencies.—The first problem, frequently a difficult one, in the application of the spectra of polyatomic molecules is to make use of the infra-red and Raman spectra to assign frequencies to the various normal modes of vibration of the molecule. An obvious necessity is, of course, that the structure of the molecule should be known or postulated. Since a proper assignment will not be possible if the chosen structure is incorrect, the spectra may be regarded, in a sense, as providing evidence for or against a particular structure. From the observed lines in both infra-red and Raman spectra, it is necessary to choose those which represent the fundamental frequencies, as distinct from the overtones and combination tones, and then to associate each one of them with a particular vibrational mode.

This task is facilitated by making use of a number of theoretical and empirical rules. Such facts as the intensities of the lines, the type of rotational structure or envelope, the presence or absence of a given line in both Raman and infra-red spectra, the degree of depolarization of Raman lines, the selection rules, and numerical relationships between the frequencies of various vibration bands can all be utilized. Further, in a polyatomic molecule no frequency over about 3700 cm.^{-1} can correspond to a fundamental band, while if there is no C—H bond the upper limit is about 2500 cm.^{-1} . As will be seen in Section 38d, certain groups may dominate a

particular mode of vibration of the molecule, so that the presence of the corresponding lines indicates the vibrations involving those groups. The distinction, which can sometimes be made, between valence and deformation vibrations is often helpful; as a general rule, the vibrations involving the stretching of valence bonds have higher frequencies than those in which the bending of such bonds is concerned. In certain rare cases a fundamental vibration frequency may be inactive in both infra-red and Raman spectra; in this case its value is generally estimated from the frequencies of combination bands.

An additional source of information, which is often important, is based on the use of isotopic molecules. If one of the atoms of a symmetrical molecule is replaced by its isotope, the symmetry disappears, and many vibrations which were previously inactive now become active in the infra-red and Raman spectra. Further, vibrations which were previously degenerate may become nondegenerate, as will be seen shortly.

38b. Internuclear Distances.¹⁰—When an analysis of vibration-rotation or rotation bands can be made, so that the separation of successive lines can be evaluated, it is possible to determine the moments of inertia, as already shown. From them, the shape and dimensions of the molecule can be calculated in many cases; some of these may be examined here. Consider, for example, the molecule of carbon dioxide; the spectra correspond to those to be expected for a symmetrical linear molecule OCO. The moment of inertia derived from the frequency separation of the vibrational lines, after allowing for the fact that alternate lines are missing, is 70.8×10^{-40} g. cm.² Since the molecule is linear, this gives a value of 1.15 Å for the C—O bond distance. Another linear triatomic molecule which is, however, not symmetrical, is hydrogen cyanide; the moment of inertia has been found to be 18.7×10^{-40} g. cm.², and this gives the C—H internuclear distance as 1.06 Å, while the C—N distance is 1.15 Å.

The spectra, as well as other properties of the water molecule, indicate an angular structure; the molecule is an asymmetrical top, and the three moments of inertia, estimated for the hypothetical vibrationless state of the molecule, are $A = 1.0229 \times 10^{-40}$, $B = 1.9207 \times 10^{-40}$ and $C = 2.9436 \times 10^{-40}$ g. cm.² Since the water molecule is flat, the moment of inertia C is equal to the sum of A and B . The observed moments of inertia are found to be compatible with a bond angle of $104^\circ 31'$ and an O—H bond distance of 0.958 Å.¹¹

As already indicated, the molecule of ammonia is pyramidal in shape, the three hydrogen atoms lying in a plane with the nitrogen atom above (or below) it. The moment of inertia about the axis perpendicular to the symmetry axis is 2.78×10^{-40} g. cm.², and this result, taken in conjunction with 0.39 Å for the height derived from the doublet separation referred to in Section 37a, leads to the following dimensions: N—H distance 1.01 Å, H—H distance 1.61 Å, bond angle 108° .

¹⁰ For summaries, see Kohlrausch, ref. 1; Sutherland, ref. 1; Wu, ref. 1.

¹¹ Dennison and Darling, *Phys. Rev.*, 57, 128 (1940).

In some cases, where several internuclear distances are involved, it is not possible to derive the interatomic dimensions uniquely from the moments of inertia obtained from the spectra. A case in point is that of ethylene; the three moments of inertia are $A = 5.70 \times 10^{-40}$, $B = 2.75 \times 10^{-40}$ and $C = 33.2 \times 10^{-40}$ g. cm.², but the C—H and C—C (double bond) distances, and the bond angles cannot be derived from them without making an assumption. If the C—H distance is taken to be 1.08 Å, which lies between the values found in acetylene (1.06 Å) and methane (1.09 Å), the C—C distance in ethylene is found to be 1.33 Å; the H—C—H bond angle is then 118°.

38c. Force Constants.¹²—One of the most interesting applications of the spectra of polyatomic molecules, from the viewpoint of the chemist, is the evaluation of the restoring force constants associated with various bonds. Such calculations have been described in Section 29g for diatomic molecules, but they are naturally much more complicated for polyatomic molecules. The results are usually approximate, for they are based on certain assumptions concerning the type of force field operative in the molecule. With a diatomic molecule there is one vibration, and since the potential energy can be expressed in terms of a single force constant, the latter can be derived, if the frequency is known; the only approximation necessary is that the oscillations must be taken as harmonic. The potential energy for a polyatomic molecule involves a number of force constants; thus, equation (34.2) may be put in the form

$$V = \frac{1}{2}(f_1 q_1^2 + f_2 q_2^2 + \cdots + 2f_{12} q_1 q_2 + 2f_{23} q_2 q_3 + \cdots), \quad (38.1)$$

where the force constants f_1, f_2 , etc., and the interaction constants f_{12}, f_{23} , etc., are used in place of the b_{ij} terms; the q_1, q_2 , etc., represent the displacements of the various atoms in the course of a vibration. The vibrational kinetic energy can be written in terms of an equation analogous to (38.1); thus, if a sufficient number of normal vibration frequencies of the molecule were available, from a study of its spectra, it should be possible to solve the secular determinantal equation (34.11) in order to derive the b_{ij} 's, that is, the force constants. The difficulty in this calculation arises from the fact that a molecule has only $3n - 6$ vibrational modes; hence, this is the maximum number of frequencies that can be known, whereas equation (38.1) may contain many more unknown force constants. The solution of the secular determinant is thus not possible without some simplification.

One method is to postulate a particular type of force field, so that the potential function involves a smaller number of force constants. Two such

¹² Van Vleck and Cross, *J. Chem. Phys.*, **1**, 357 (1933); Howard, *ibid.*, **3**, 207 (1935); Bonner, *ibid.*, **5**, 293 (1937); Wall and Glockler, *ibid.*, **5**, 813 (1937); Wu and Kiang, *ibid.*, **7**, 178 (1939); Stitt, *ibid.*, **7**, 297 (1939); Linnett, *ibid.*, **8**, 91 (1940); Crawford and Brinkley, *ibid.*, **9**, 69 (1941); Wells and Wilson, *ibid.*, **9**, 314, 319 (1941); Rosenthal, *Phys. Rev.*, **46**, 730 (1934); Sutherland and Dennison, *Proc. Roy. Soc., A*, **148**, 250 (1935); Penney and Sutherland, *ibid.*, **156**, 654 (1936); Conn and Sutherland, *ibid.*, **172**, 172 (1939); Thompson and Linnett, *J. Chem. Soc.*, 1291, 1376, 1384 (1937).

force fields have been proposed: one is the *central force field*, according to which the restoring force acting on an atom displaced from its equilibrium position depends only on the magnitude of the displacement, and not on its direction. The second type of force field, the *valence force field*, is, at least as a first approximation, in harmony with what may be expected from chemical considerations; it postulates two kinds of restoring force, namely, those which tend to prevent stretching of the valence bonds and those which operate against the bending of such bonds. The potential function for the valence force field thus becomes

$$V = \frac{1}{2} \{ k_1(\Delta d_1)^2 + k_2(\Delta d_2)^2 + \cdots + k_{\theta_1}(\Delta \theta_1)^2 + k_{\theta_2}(\Delta \theta_2)^2 + \cdots \} \quad (38.2)$$

where Δd_1 , Δd_2 , etc., are the displacements of the nuclei in the directions of the valence bonds, and $\Delta \theta_1$, $\Delta \theta_2$, etc., are the changes in the bond angles; k_1 , k_2 , etc., and k_{θ_1} , k_{θ_2} , etc., are the respective force constants. In this way the number of unknowns is generally reduced below the number of known vibration frequencies, and so the secular equation can be solved to give the force constants. The test of the validity of the latter is that they may be used to reproduce with sufficient accuracy a larger number of vibration frequencies than the derived force constants. If the agreement is not satisfactory, additional terms (cross terms), which are completely absent from equation (38.2), may be added to the potential function; in this manner better values of the force constants can be calculated.

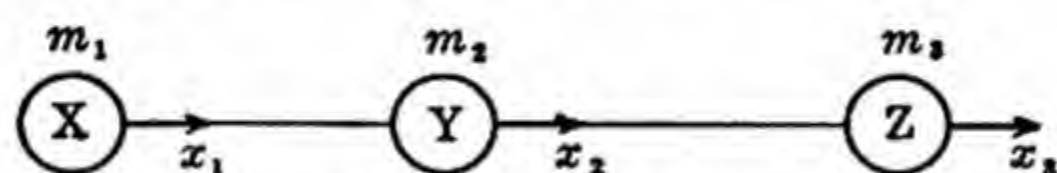


FIG. 30. Vibrating unsymmetrical linear XYZ molecule

The procedure may be illustrated by reference to some simple cases. Consider the linear unsymmetrical molecule XYZ, as shown in Fig. 30; let m_1 , m_2 and m_3 be the masses of the three atoms, and let x_1 , x_2 and x_3 be their respective displacements in the course of vibration. The complete potential function is then

$$V = \frac{1}{2} (f_1 x_1^2 + f_2 x_2^2 + f_3 x_3^2 + 2f_{12} x_1 x_2 + 2f_{13} x_1 x_3 + 2f_{23} x_2 x_3), \quad (38.3)$$

in which there are six unknown, and different, force constants. The linear triatomic molecule has four vibrational modes, of which two are identical; there are thus available three frequencies only for the determination of six unknowns. The problem is simplified by assuming a valence force field to be operative; the potential function may then be written

$$V = \frac{1}{2} \{ k_1(\Delta r_1)^2 + k_2(\Delta r_2)^2 + k_{\theta}(\Delta \theta)^2 \}, \quad (38.4)$$

where k_1 and k_2 are the force constants of the X—Y and Y—Z bonds, respectively, and Δr_1 and Δr_2 represent the changes in the corresponding bond lengths; k_{θ} is the force constant for the bending vibration and $\Delta \theta$ is the change

in angle $X-Y-Z$. The potential energy given by equation (38.4) is obviously an approximation, but this is unfortunately inevitable, since it involves three unknowns, and this is the maximum number permitted.

The vibrational kinetic energy of the system can be expressed as a function of r_1 , r_2 and θ , and this can be divided into two parts with no cross terms between them; one part refers to the parallel vibrations ν_1 and ν_3 , and the other to the doubly degenerate perpendicular vibration ν_2 . Similarly, the potential function, equation (38.4), can be divided into two corresponding parts; the terms involving Δr_1 and Δr_2 are dependent on the parallel vibrations, while that with $\Delta\theta$ is related to the perpendicular vibration. The third order secular determinant for this particular problem thus reduces to a quadratic, involving λ_1 and λ_3 , and a linear equation in λ_2 , where λ is defined as $4\pi^2\nu^2$ [cf. equation (34.9)].

For the parallel vibrations, equation (38.4) gives for the potential energy

$$V_r = \frac{1}{2}\{k_1(\Delta r_1)^2 + k_2(\Delta r_2)^2\}, \quad (38.5)$$

and the expression for the corresponding kinetic energy can be shown to be

$$T_r = \frac{1}{2M}\{m_1(m_2 + m_3)(\dot{\Delta r}_1)^2 + 2m_1m_3\dot{\Delta r}_1\dot{\Delta r}_2 + m_3(m_1 + m_2)(\dot{\Delta r}_2)^2\}, \quad (38.6)$$

where M is equal to $m_1 + m_2 + m_3$. The secular equation, corresponding to the determinantal equation (34.11), is now

$$\begin{vmatrix} b_{11} - a_{11}\lambda & b_{12} - a_{12}\lambda \\ b_{12} - a_{12}\lambda & b_{22} - a_{22}\lambda \end{vmatrix} = 0,$$

and in the present case this becomes, after reversing signs,

$$\begin{vmatrix} \frac{m_1}{M}(m_2 + m_3)\lambda - k_1 & \frac{m_1m_3}{M}\lambda \\ \frac{m_1m_3}{M}\lambda & \frac{m_3}{M}(m_1 + m_2)\lambda - k_2 \end{vmatrix} = 0. \quad (38.7)$$

The solutions of this determinant are given by

$$\lambda_1\lambda_3 = \frac{M}{m_1m_2m_3} k_1k_2 \quad (38.8)$$

and

$$\lambda_1 + \lambda_3 = \frac{m_1 + m_2}{m_1m_2} k_1 + \frac{m_2 + m_3}{m_2m_3} k_2, \quad (38.9)$$

where

$$\lambda_1 = 4\pi^2\nu_1^2 \quad \text{and} \quad \lambda_3 = 4\pi^2\nu_3^2,$$

ν_1 and ν_3 being the frequencies of the parallel normal vibrations of the XYZ molecule. If these frequencies are known from the infra-red or Raman spectra, the force constants k_1 and k_2 can be evaluated.

For the perpendicular (bending) vibration, the appropriate portion of equation (38.4) for the potential energy is

$$V_\theta = \frac{1}{2}k_\theta(\Delta\theta)^2, \quad (38.10)$$

and the corresponding kinetic energy is

$$T_\theta = \frac{r_1 r_2}{2I} \cdot \frac{m_1 m_2 m_3}{M} (\Delta\dot{\theta})^2, \quad (38.11)$$

where I is the moment of inertia of the molecule, given by

$$I = \frac{1}{M} \{m_1(m_2 + m_3)r_1^2 + 2m_1 m_3 r_1 r_2 + m_3(m_1 + m_2)r_2^2\}.$$

The (linear) secular equation is now

$$\begin{aligned} \frac{r_1 r_2}{I} \cdot \frac{m_1 m_2 m_3}{M} \lambda_2 - k_\theta &= 0, \\ \therefore \lambda_2 &= \frac{I}{r_1 r_2} \cdot \frac{M}{m_1 m_2 m_3} k_\theta, \end{aligned} \quad (38.12)$$

where

$$\lambda_2 = 4\pi^2\nu_2^2.$$

From equation (38.12), therefore, the deformation (bending) force constant k_θ can be determined, utilizing the known value of ν_2 , the doubly degenerate perpendicular frequency.

If the linear triatomic molecule is symmetrical, viz., XYX , then the valence force constants k_1 and k_2 are equal, and so also are the displacements Δr_1 and Δr_2 ; in this event, therefore, the potential function, equation (38.4), becomes

$$V = \frac{1}{2}\{2k_1(\Delta r_1)^2 + k_\theta(\Delta\theta)^2\}.$$

There are now two unknown force constants, but since there are still available three frequencies, it is possible to improve the potential function by the inclusion of an additional term, namely the cross term $k_{13}\Delta r_1\Delta r_2$, so that the potential energy may be written as

$$V = \frac{1}{2}\{2k_1(\Delta r_1)^2 + 2k_{13}\Delta r_1\Delta r_2 + k_\theta(\Delta\theta)^2\}. \quad (38.13)$$

If the treatment described above is applied to equation (38.13), the force constant for the bending vibration is unchanged, except that m_1 and m_3 are equal; for the valence vibrations ν_1 and ν_3 , it is now found that

$$\lambda_1 \lambda_3 = \frac{2m_1 + m_2}{m_1^2 m_2} (k_1^2 - k_{13}^2)$$

and

$$\lambda_1 + \lambda_3 = \frac{2(m_1 + m_2)}{m_1 m_2} k_1 - \frac{2}{m_2} k_{13},$$

where m_1 is the mass of each of the two identical end atoms, and m_2 is that of the central atom.

In general, the procedure for evaluating force constants is similar to that described above; the potential function is written out and as many cross terms as are permitted by the known normal vibration frequencies are included. The expression for the vibrational kinetic energy is often complicated, but this is essentially a problem in mechanics. With the equations for the potential (V) and kinetic (T) energies available, the secular determinant may be set up, and solved for the λ 's in terms of the k 's, the force constants. The determinant of high order may be reduced to a number of simpler determinants by making use of the symmetry of the vibrations, as shown in the case of the examples given above. Before this can be done it is, of course, necessary to make a proper assignment of the observed spectral frequencies to the appropriate normal vibrations. For a molecule containing a fairly large number of atoms it is not always possible to do this with certainty. However, if the proper assignment has been made, and the frequencies are known, the force constants attributed to various valence bonds can then be evaluated.

The spectra of isotopic molecules provide, at least in principle, a method for calculating improved force constants; these are supposed to remain unchanged (cf. Section 29h) when one isotopic atom is replaced by another. The extra frequencies, derived from the spectra of the isotopic forms, provide additional information for the solution of the secular equation. If the force constants calculated for one isotopic molecule are correct, they must be able to reproduce with reasonable accuracy the observed frequencies for the other isotopic form. Another advantage of isotopic exchange is that it often introduces new frequencies as a result of the alteration in the symmetry characteristics of the molecule. Methane, CH_4 , for example, has only four different frequencies, three being degenerate; however, for the isotopic form $\text{C}_2\text{H}_2\text{D}_2$ there are nine nondegenerate vibrations.

The force constants derived by the foregoing method cannot have a precise significance, as they are based on the assumption of a special type of relatively simple force field. The results are nevertheless of interest, since the valence force field cannot differ very greatly from that actually existing in a molecule in which the atoms are held together by valence forces.

TABLE XIII. VALENCE BOND FORCE CONSTANTS IN DYNES PER CM.

Bond	Force Constant	Bond	Force Constant	Bond	Force Constant
C—C	4.6×10^6	C—O	4.9×10^5	C—N	4.8×10^6
C=C	9.5	C=O	12.3	C=N	12.1
C≡C	15.8	C≡O	18.6	C≡N	17.5

From the study of a number of molecules, it appears that the force constant of a given valence bond is almost constant in different compounds, although, as may be anticipated, the remainder of the molecule exerts some perturbing effect. The existence of resonance, which alters the nature of the bond, has an important influence; hence, force constants may be utilized

to detect such resonance. Some mean, approximate, values for the force constants of single, double and triple bonds are recorded in Table XIII. The C—H force constant is 5.0×10^5 dynes per cm. It is of interest to note that the force constants increase approximately in proportion to the multiplicity of the bond.

The application of the results in Table XIII may be illustrated by reference to one or two cases. In carbon dioxide, for example, the force constant of the carbon-oxygen bonds is found, from the spectrum of this gas, to be 15.2×10^5 dynes per cm.; it is evident that in this substance these linkages have both double and triple bond character. Similar considerations apply to carbon suboxide, C_3O_2 , in which the force constant of the carbon-carbon bond is 14.9×10^5 , while that of the carbon-oxygen bond is 14.2×10^5 dynes per cm. In this substance there is evidently resonance between double bonded and triple bonded structures.

38d. Characteristic Bond Frequencies.—Although the frequencies derived from infra-red and Raman spectra are for the normal vibrations of the molecule as a whole, it is often true that the force constants of certain linkages virtually control some of the vibrational modes. The presence of particular bonds may thus be associated with certain, approximately constant, frequencies even in different molecules. As a result it has become the practice to associate a characteristic frequency with each type of linkage; it must be emphasized that this is only an approximation, but it is one which has proved useful. Apart from bonds, such as C—H, N—H and O—H, which have characteristic frequencies of about 3000 cm.^{-1} , single bonded linkages, e.g., C—C, C—N and C—O, have frequencies in the vicinity of 800 to 900 cm.^{-1} . The characteristic frequency of a double bond is about 1600 to 1700 cm.^{-1} , while that of a triple bond is in the region of 2100 cm.^{-1} . For heavier atoms, the frequencies are somewhat less.

The use of characteristic frequencies may be illustrated by reference to the isocyanide group; substances containing this grouping invariably give a spectral line of frequency approximately 2150 cm.^{-1} . It follows, therefore, that the triple bonded $\text{—N}\equiv\text{C}$ grouping must make an important contribution to the structure of isocyanide compounds.

CHAPTER VI

THE ELECTRONIC CONFIGURATIONS OF DIATOMIC MOLECULES ¹

ELECTRONIC STATES OF MOLECULES AND ATOMS

39a. Dissociation of Molecules.—When a molecule dissociates it may give rise to normal atoms or to one or more excited atoms; the state of the product is dependent, to some extent, on the electronic state of the original molecule, and consideration will now be given to this and related subjects. The results obtained are important in connection with the problems of molecular structure. Three lines of approach have proved of value in providing information on the subjects of immediate interest. First, it may be supposed that two atoms in known electronic states are brought together until they form a molecule. Second, the nuclei of the atoms forming a diatomic molecule are assumed to be brought so close to each other that they fuse to form what is called a *united atom*, with the same number of electrons as the molecule; the united atom is then split up, hypothetically, until it forms the given molecule. Third, by adopting a procedure similar to that used in the elucidation of the electronic configuration of atoms, it is supposed that the electrons are added one by one to the system consisting of two fixed nuclei.

39b. Combination of Separated Atoms to Form Diatomic Molecules.—The possible molecular states that may arise from bringing together two atoms, have been derived theoretically from quantum mechanics. These states are not necessarily all observed, but at least all states that are theoretically possible can be found for any particular pair of atoms. Suppose L_1, S_1 and L_2, S_2 represent the orbital and spin angular momentum quantum numbers of two atoms which are brought up to one another. As the nuclei approach, an electric field is produced (cf. Section 2a) in the direction of the internuclear axis, and there is a space quantization of the angular momenta with reference to this direction. Suppose Λ_1 and Λ_2 are the quantum numbers corresponding to L_1 and L_2 , respectively, then according to equation (2.1) their possible values are given by

$$\Lambda_1 = L_1, L_1 - 1, L_1 - 2, \dots, -L_1$$

and

$$\Lambda_2 = L_2, L_2 - 1, L_2 - 2, \dots, -L_2.$$

¹ Herzberg, "Molecular Spectra and Molecular Structure: Diatomic Molecules"; Kronig, 'Optical Basis of the Theory of Valency'; Mulliken, *Rev. Mod. Phys.*, 4, 1 (1932); Van Vleck and Sherman, *ibid.*, 7, 167 (1935).

The permitted values for the quantum number Λ for the resultant orbital angular momentum are then obtained by vector combination of Λ_1 and Λ_2 ; thus

$$\Lambda = |\Lambda_1 + \Lambda_2| \\ = L_1 + L_2, L_1 + L_2 - 1, L_1 + L_2 - 2, \dots, |L_1 - L_2|, \quad (39.1)$$

positive values only being permitted. As already mentioned (Sections 2a, 30f), states for which Λ is not zero are doubly degenerate.

Consider, for example, the combination of two atoms in P states; L_1 and L_2 are both unity, and so the possible values of Λ are 2, 1 and 0, corresponding to Δ , Π and Σ states, respectively. The number of states of each type may be derived by vector addition, or by means of group theory. If the number of Σ states is even, then half of these will be positive (Σ^+) and the other half are negative (Σ^-), in the sense defined in Sections 2e and 31a. If there are an odd number of Σ states, the distribution is found by the following rule. If the sum $L_1 + L_2 + \sum l_1 + \sum l_2$ is even, the number of Σ^+ states is one larger than the number of Σ^- states, but if the sum is odd there is one more Σ^- state. The $\sum l_1$ and $\sum l_2$ terms refer to the sum of the l values for all the electrons in the atoms represented by the subscripts 1 and 2, respectively. For the combination of a P_u atom with another P_u atom, both $\sum l_1$ and $\sum l_2$ are odd (cf. Section 1g), and since L_1 and L_2 are both unity, it follows that $L_1 + L_2 + \sum l_1 + \sum l_2$ is even, and the number of Σ^+ states will exceed the Σ^- states by unity. A similar result will clearly be obtained with two atoms in P_g states, but if one atom is P_u and the other P_g there will be one Σ^- state more than the number of Σ^+ states.

TABLE XIV. MOLECULAR STATES FORMED BY UNLIKE ATOMS

Separated Atoms			Molecular States
$S_g + S_g$	or	$S_u + S_u$	Σ^+
	$S_g + S_u$		Σ^-
$S_g + P_g$	or	$S_u + P_u$	Σ^-, Π
$S_g + P_u$	or	$S_u + P_g$	Σ^+, Π
$S_g + D_g$	or	$S_u + D_u$	Σ^+, Π, Δ
$S_g + D_u$	or	$S_u + D_g$	Σ^-, Π, Δ
$P_g + P_g$	or	$P_u + P_u$	$\Sigma^+(2), \Sigma^-, \Pi(2), \Delta$
	$P_g + P_u$		$\Sigma^+, \Sigma^-(2), \Pi(2), \Delta$
$P_g + D_g$	or	$P_u + D_u$	$\Sigma^+, \Sigma^-(2), \Pi(3), \Delta(2), \Phi$
$P_g + D_u$	or	$P_u + D_g$	$\Sigma^+(2), \Sigma^-, \Pi(3), \Delta(2), \Phi$
$D_g + D_g$	or	$D_u + D_u$	$\Sigma^+(3), \Sigma^-(2), \Pi(4), \Delta(3), \Phi(2), \Gamma$
	$D_g + D_u$		$\Sigma^+(2), \Sigma^-(3), \Pi(4), \Delta(3), \Phi(2), \Gamma$

Although the results are the same in principle, whether the two nuclei of the atoms which together make up a molecule have equal charges or not, it is convenient to consider the two types separately, since in the former case g and u states of the molecule are possible. The molecular states resulting when two unlike separated atoms are brought together are recorded in Table XIV; in view of the large number of possibilities arising from atoms

in F states, these are omitted, especially as they occur only infrequently with normal atoms. The numbers in parentheses in Table XIV give the number of states of the particular type.²

The multiplicity of the different states can be derived by considering the resultant spin. If the type of coupling is that hitherto assumed for atoms (LS), that is close coupling of the orbital angular momenta among themselves, and similarly close coupling of the spin momenta (cf. Section 1e), the resultant spin of the molecule is obtained by vector addition of the separate resultant spins of the two atoms. If the latter are S_1 and S_2 , then the possible values of the spin quantum number S of the diatomic molecule are

$$S = S_1 + S_2, S_1 + S_2 - 1, S_1 + S_2 - 2, \dots, |S_1 - S_2|. \quad (39.2)$$

The multiplicity of each state, resulting from the splitting in the magnetic field due to the orbital motion of the electrons, is $2S + 1$, as shown in Section 2b, and so every state given in Table XIV, as derivable from a given pair of atoms, will occur with a multiplicity of $2S + 1$ for every possible S value obtained from equation (39.2).

The application of these rules may be illustrated by considering the approach of a normal (3P) carbon atom to a normal (4S) nitrogen atom to form the spectroscopically stable CN molecule. The electronic structure of the 3P carbon atom is $1s^2 2s^2 2p^2$, and that of the 4S nitrogen atom is $1s^2 2s^2 2p^3$. For the carbon atom L_1 is 1 and $\sum l_1$ is 2, since l is zero for s electrons and unity for p electrons; for the nitrogen atom L_2 is 0 and $\sum l_2$ is 3. Hence $L_1 + L_2 + \sum l_1 + \sum l_2$ is even, and the number of Σ^+ states must be one greater than the number of Σ^- states. Reference to Table XIV shows that the combination of an atom in an S state with one in a P state gives Σ and Π as possible molecular states; in the case under consideration these must be Σ^+ and Π . From the multiplicities of the atomic terms, it is evident that for carbon S_1 is 1, and for nitrogen S_2 is $\frac{3}{2}$; hence the possible values of the resultant spin quantum number of the CN molecule are given by equation (39.2) as $\frac{5}{2}$, $\frac{3}{2}$ and $\frac{1}{2}$, corresponding to multiplicities of 6, 4 and 2, respectively. It follows, therefore, that the possible molecular states of CN derived from a 3P carbon atom and a 4S nitrogen atom are $^6\Sigma^+$, $^4\Sigma^+$, $^2\Sigma^+$, $^6\Pi$, $^4\Pi$ and $^2\Pi$; of these, $^2\Sigma^+$, the ground state, and $^2\Pi$ are known. Mention may be made of the fact that diatomic molecular states with multiplicities greater than three are rarely observed.

39c. Combination of Atoms with Equal Nuclear Charges.—When a molecule is formed from two atoms with nuclei carrying equal charges, it is necessary to distinguish between g and u states (Sections 2e, 31b). If the two atoms are brought together in the same electronic state, e.g., both 1S or both 2P , etc., the possible molecular states are the same as given in Table XIV for unlike atoms; some of the states, however, have g and others have u character. The actual properties depend on the resultant spin, and

² Wigner and Witmer, *Z. Physik*, 51, 859 (1928); Mulliken, ref. 1.

hence on the multiplicity, of the molecular state; the results for various simple cases, derived by means of group theory, are recorded in Table XV. According to the tabulation, two nitrogen atoms in the (4S) ground state should be able to produce the molecular states $^1\Sigma_g^+$, $^3\Sigma_u^+$, $^5\Sigma_g^+$ and $^7\Sigma_u^+$; as may be expected, the first two states only have been observed, the others having higher multiplicities than generally occur in practice.³

TABLE XV. MOLECULAR STATES FORMED BY ATOMS WITH EQUAL NUCLEAR CHARGES

Separated Atoms	Molecular States
$^1S + ^1S$	$^1\Sigma_g^+$
$^2S + ^2S$	$^1\Sigma_g^+, ^3\Sigma_u^+$
$^3S + ^3S$	$^1\Sigma_g^+, ^3\Sigma_u^+, ^5\Sigma_g^+$
$^4S + ^4S$	$^1\Sigma_g^+, ^3\Sigma_u^+, ^5\Sigma_g^+, ^7\Sigma_u^+$
$^1P + ^1P$	$^1\Sigma_g^+(2), ^1\Sigma_u^-, ^1\Pi_g, ^1\Pi_u, ^1\Delta_g$
$^2P + ^2P$	$^1\Sigma_g^+(2), ^1\Sigma_u^-, ^3\Sigma_u^+(2), ^3\Sigma_g^-, ^1^3\Pi_g, ^1^3\Pi_u, ^1\Delta_g, ^3\Delta_u$
$^3P + ^3P$	$^1^5\Sigma_g^+(3), ^1^5\Sigma_u^-, ^3\Sigma_u^+(2), ^3\Sigma_g^-, ^1^3^5\Pi_g, ^1^3^5\Pi_u, ^1^5\Delta_g, ^3\Delta_u$
$^1D + ^1D$	$^1\Sigma_g^+(3), ^1\Sigma_u^-(2), ^1\Pi_g(2), ^1\Pi_u(2), ^1\Delta_g(2), ^1\Delta_u$, etc.
$^2D + ^2D$	As for $^1D + ^1D$, and $^3\Sigma_u^+(3), ^3\Sigma_g^-(2), ^3\Pi_u(2), ^3\Pi_g(2), ^3\Delta_u(2), ^3\Delta_g$, etc.
$^3D + ^3D$	As for $^1D + ^1D$ and $^2D + ^2D$, and quintets corresponding to the singlets.

If the two atoms of equal nuclear charge are in different electronic states, then a resonance occurs between the two forms of the system; in one form the excitation energy is associated with one atom, and in the other form it is associated with the other atom. As a result of this resonance each molecular state can appear twice, once as a g term and once as a u term (cf. Section 31b). The possible molecular states are identical with those recorded in Table XIV for unlike atoms, with the modification that each can occur with both g and u character. For example, in the combination of two atoms with equal nuclear charges, one being in an S_g state and the other in a D_u state, the following molecular states are theoretically possible: Σ_g^+ , Σ_u^+ , Π_g , Π_u , Δ_g and Δ_u . The permitted multiplicities of the various states are derived in the usual manner from the resultant spin of the molecule.

39d. Splitting of the United Atom.—If the two nuclei in the spectroscopically stable diatomic molecule CH were made to coalesce, the resulting united atom would be equivalent to a nitrogen atom. Useful information can be obtained by carrying through the purely imaginary process of splitting the nucleus of a nitrogen atom into the nuclei of carbon and hydrogen. For a small splitting, the effect on the orbital and spin angular momenta is the same as that of an electric field. The respective vectors L and S of the united atom are thus space quantized with respect to the direction of the field, i.e., the internuclear axis of the molecule. The possible values of the quantum number of the component of the orbital angular momentum in

³ Wigner and Witmer, ref. 2; Mulliken, ref. 1.

this direction are then given by

$$\Lambda = L, L - 1, L - 2, \dots, 2, 1, 0. \quad (39.3)$$

The states of the diatomic molecule that may arise from a particular united atom can thus be derived from a knowledge of the state of the latter. For Σ states, the positive or negative character is determined by the value of $L + \sum l$ for the united atom; if this is even then the state is Σ^+ , but if it is odd then a Σ^- state should result.

The spin vector of the united atom, represented by the quantum number S , is already a component in the direction of an electric field; this remains unchanged when the nucleus is split to form a diatomic molecule. The multiplicity of each state of the latter is thus the same as that of the united atom.

The nitrogen atom in its ground state is a $4S_u$ term, and there are $2D_u$ and $2P_u$ states with slightly higher energies. Consider first the $4S$ state; since L for the united atom is zero (for an S state), the only possible value of Λ for the CH molecule produced by splitting the nitrogen nucleus is also zero. The multiplicity, as just stated, is unaffected and so the diatomic CH molecule should exist in a 4Σ state. For the normal $4S_u$ nitrogen atom, $\sum l$ is odd, since it is a u state, and L is zero; it follows, therefore, that the molecular state must be negative, i.e., $4\Sigma^-$. From the $2D_u$ state of the nitrogen atom, the possible forms of the CH molecule are 2Δ , 2Π and $2\Sigma^-$, the negative symmetry character of the 2Σ term follows from the fact that $L + \sum l$ is odd for the $2D_u$ nitrogen atom. In the same way, it can be shown that the $2P_u$ nitrogen atom should give rise to 2Π and $2\Sigma^+$ states of the CH molecule.

From the foregoing discussion, therefore, it is evident that the following states of the physically stable, but chemically unstable, CH molecule should be theoretically possible: $4\Sigma^-$, 2Δ , $2\Pi(2)$, $2\Sigma^-$ and $2\Sigma^+$; of these, 2Δ , $2\Pi(1)$, $2\Sigma^-$ and $2\Sigma^+$ have been observed in various spectra. As will be seen later, the second 2Π state is probably unstable physically, and hence it is not readily detected. Since states of high multiplicity are uncommon among diatomic molecules, it is not surprising that the $4\Sigma^-$ state has not been observed. In any event ordinary (dipole) transitions from the 4Σ state to the other states are forbidden, because of the difference in multiplicity (cf. Section 31f), and so the former would not normally be detected spectroscopically.

If the nucleus of the united atom is split into two nuclei of equal charge, then the possible states of the molecule are the same as for unlike nuclei, with the g or u symmetry character added. The conclusion has been reached, by theoretical arguments, that the molecular states are all g or all u , according as the united atom is g or u . The sulfur atom, for example, has a $3P_g$ ground term; if this is treated as a united atom corresponding to the oxygen molecule, the possible states of the latter are found to be $3\Pi_g$ and $3\Sigma_g^-$, utilizing the rules give above. The normal state of molecular oxygen is, in fact, $3\Sigma_g^-$.

MOLECULAR ORBITALS ⁴

40a. Electron Orbitals in Molecules: The United Atom.—In order to facilitate the study of the development of the electronic structure of a molecule as the electrons are added to the nuclei, one by one, it is convenient to construct a system of quantum numbers that are applicable to the molecular case. When moving in a field of central symmetry, such as exists in an atom, the state of an electron, apart from its spin, may be described in terms of four quantum numbers, n , l , m_l and m_s , as seen in Section 1. In a molecule, however, the resultant field due to the nuclei and the electrons, other than the one under consideration, is no longer centrally symmetric; in these circumstances the quantum numbers n and l no longer have an exact significance.

The quantum number m_l of the electron, representing the component of the orbital angular momentum l in the direction of the applied electric field, i.e., along the direction of the internuclear axis of the molecule, remains strictly defined in the molecule as well as in the atom. In the treatment of molecules this quantum number is indicated by the symbol λ , and the possible values are given by

$$\lambda = l, l - 1, l - 2, \dots, 2, 1, 0. \quad (40.1)$$

In the electric field, states with $\lambda = +l$ have the same energy as those with $\lambda = -l$; hence, it is not necessary to treat $+l$ and $-l$, and similarly for other cases, as separate quantum numbers, but it will be understood that all levels except the one with $\lambda = 0$ are doubly degenerate. For purposes of representation, electrons (or orbitals) ⁵ with λ equal to 0, 1, 2, 3, etc., are indicated by the lower case Greek letters σ , π , δ , ϕ , etc.

The electron spin is not influenced by an electric field, and hence the spin vector is not affected in molecule formation. The value of m_s in the molecule or united atom states is therefore the same as in the separated atom.

In spite of the uncertainty involved, it is necessary that two quantum numbers be used in addition to λ and the spin quantum number, in order to distinguish an electron orbital in a molecule. As stated above, the atomic quantum numbers n and l are really no longer significant for a molecule; nevertheless, provided the two nuclei are close together, i.e., the state approaches that of the united atom, the departure of the field from central symmetry is not considerable, and the quantum numbers n and l ascribed to the electron in the united atom may still be regarded as applicable in the molecule. The values of n and l for the molecular electron orbital are indicated in the same manner as for atomic electrons; an integer represents the value of n , and this is followed by one of the letters s , p , d , f , etc., for l

⁴ Hund, *Z. Physik*, 51, 759 (1928); 63, 719 (1930); Mulliken, *Phys. Rev.*, 32, 186, 761 (1928); 33, 730 (1929); ref. 1; Lennard-Jones, *Trans. Faraday Soc.*, 25, 668 (1929); Herzberg, *Z. Physik*, 57, 601 (1929).

⁵ In the following treatment the terms "electron" and "orbital" are used more or less interchangeably; as a rule no distinction is made between the orbital and the electron occupying the orbital.

values of 0, 1, 2, 3, etc., respectively. Thus, if n is 2 and l is 1 for an electron in the united atom, it will be a $2p$ atomic electron; in the formation of the diatomic molecule whose nuclei are close together, it may become either a $2p\sigma$ electron ($\lambda = 0$) or a $2p\pi$ electron ($\lambda = 1$). There are no other possibilities, since λ must be either 1 or 0 with $l = 1$. Because of the restriction in the values of λ , as stated in equation (40.1), and the restriction upon the value of l , it follows that s atomic electron orbitals can give rise only to $s\sigma$ orbitals in the diatomic molecule; p electrons yield $p\sigma$ and $p\pi$; d electrons produce $d\sigma$, $d\pi$ and $d\delta$ electrons in the molecule.

The number of electrons of any particular type that can be present in a molecule is restricted by the Pauli principle (Section 1c), for no two electrons can have the same four quantum numbers. If the molecule approximates to the united atom, then n and l may be regarded as being definite; under these conditions, it follows that for a given n and l , no two electrons can have the same values of λ unless their spins are opposed. If λ is zero, that is for σ electrons, the spin component m_s , which is unaffected by molecule formation, as mentioned above, can thus be either $+\frac{1}{2}$ or $-\frac{1}{2}$. For a fixed n and l , therefore, there cannot be more than two σ electrons. Electrons having the same numerical values of n , l and λ are said to be *equivalent*; a diatomic molecule therefore cannot have more than two equivalent σ electrons. In other words, the configuration σ^2 , for example, as in $(1s\sigma)^2$, $(2p\sigma)^2$, etc., represents a closed shell in a molecule.

For π electrons, the value of λ may be $+1$ or -1 , the two states, as mentioned previously, having equal energies; in each case m_s may be $+\frac{1}{2}$ or $-\frac{1}{2}$, so that a diatomic molecule may have a maximum of four equivalent π electrons. That is to say, π^4 , as in $(2p\pi)^4$, $(3d\pi)^4$, etc., constitutes a closed molecular shell. Similarly, for δ electrons, λ can be $+2$ or -2 , while m_s may be $+\frac{1}{2}$ or $-\frac{1}{2}$ in each case; four equivalent δ electrons, as in $(3d\delta)^4$, would represent a closed shell in a diatomic molecule.

It is apparent from the conclusions reached in the foregoing paragraphs that electrons for which n is 1 in the united atom can only give rise to two $1s\sigma$ electrons in the molecule, i.e., a closed $(1s\sigma)^2$ group is possible; this is because the only permitted value of l , and hence of λ , is zero. For n equal to 2 in the united atom, there may be two $2s\sigma$, two $2p\sigma$ and four $2p\pi$ electron orbitals, since l and λ can now both be 1 or 0; the closed shells with principal quantum number 2 are $(2s\sigma)^2$, $(2p\sigma)^2$ and $(2p\pi)^4$. When n is 3 in the united atom, it can be readily seen that the completed electron groups in the diatomic molecule with nuclei close together are $(3s\sigma)^2$, $(3p\sigma)^2$, $(3p\pi)^4$, $(3d\sigma)^2$, $(3d\pi)^4$ and $(3d\delta)^4$. In an atom, the order of (decreasing) binding of electrons is $1s$, $2s$, $2p$, $3s$, $3p$, and this is the order in which the electron groups are completed. It is probable, therefore, that in the corresponding molecule, the binding will decrease approximately in the order $1s\sigma$, $2s\sigma$, $2p\sigma$, $2p\pi$, $3s\sigma$, $3p\sigma$, $3p\pi$; if electrons were imagined as being added one at a time, they would presumably fill these orbitals more or less in the order given.

40b. The Separated Atom State.—When the nuclei are far apart, the molecule then approaching the *separated atom* state, the numbers n and

can no longer be defined. In order to identify a molecular electron orbital under these conditions, it is convenient to consider a molecule as being formed by bringing together the two constituent atoms. The Greek letter indicating the λ value is now *followed* by the symbols for the n and l values the electron had in the separated atom system. If the two atoms are unlike, it is desirable to specify further the particular atom from which the electron originated. For example, if in the formation of a molecule AB from two atoms A and B, a $1s$ electron from atom A has a λ value of zero in the molecule, it would be described as $\sigma 1s_A$; a $2p$ electron from the atom B might become either $\sigma 2p_B$ or $\pi 2p_B$ in the molecule, at large internuclear separations.

According to the Pauli principle there can be two $1s$ electron orbitals on the separated atom A and two on the atom B, that is, two $1s_A$ and two $1s_B$ orbitals are possible in the molecule; in each atom the spin vectors of the electrons occupying each pair of orbitals must be opposed to one another. Since each of the orbitals can be associated with a σ state in the molecule, it is considered that the closed shells $(\sigma 1s_A)^2$ and $(\sigma 1s_B)^2$ are possible, provided the nuclei remain widely separated. The implication here, of course, is that $\sigma 1s_A$ and $\sigma 1s_B$ represent two different orbitals in the molecule, so that each may be occupied by two electrons having opposite spins. In the same way, the $2s$ electrons in atoms A and B will give rise to the groups $(\sigma 2s_A)^2$ and $(\sigma 2s_B)^2$ in the molecule.

From the $2p$ atomic orbitals it is possible to derive both $\sigma 2p$ and $\pi 2p$ orbitals; as usual, there will be two of the former (σ) type for each atom, making the closed shells $(\sigma 2p_A)^2$ and $(\sigma 2p_B)^2$, and four of the $\pi 2p$ type, viz., $(\pi 2p_A)^4$ and $(\pi 2p_B)^4$. The argument is here identical with that employed in the case of the molecule produced from the united atom; for a p electron, λ may be $+1$ or -1 , and hence *each* of the symbols $\pi 2p_A$ and $\pi 2p_B$ must represent two different orbitals. Since the spin component may have the quantum number $+\frac{1}{2}$ and $-\frac{1}{2}$ in each case, it follows that there can be four $\pi 2p_A$ and four $\pi 2p_B$ electrons in the molecule with large internuclear separation. A similar argument shows that a closed shell will contain four d electrons, e.g., $(\delta 3d_A)^4$ and $(\delta 3d_B)^4$.

If the nuclei of the atoms A and B have the same charge, the electrons will have the even (g) and odd (u) symmetry character, as described earlier. In the event that the molecule approximates the united atom, the g or u character is determined by its state in that atom; thus, if the l value of an electron in the united atom is even, i.e., for s and d electrons, it will have g character in the molecule with identically charged nuclei, but if l is odd, i.e., for p and f electrons, the electron will have the u property. For a molecule approaching the condition of the separated atoms carrying the same nuclear charge, there will always be two electrons having the same mean energy. For example the energy of the $\sigma 1s$ electron derived from an atom A will be identical with the $\sigma 1s$ electron from atom B, since the nuclei have equal charge; the $\sigma 1s$ state is consequently degenerate, at infinite nuclear separation. As the distance between the nuclei is decreased to some extent, interaction causes a removal of the degeneracy and two slightly different energy

states result. These can differ only in the g and u character, and hence they are denoted by the symbols $\sigma_g 1s$ and $\sigma_u 1s$, respectively.

Since $\sigma_g 1s$ and $\sigma_u 1s$ represent different orbitals, the Pauli principle leads to the conclusion that closed shells will contain two electrons of each type, viz., $(\sigma_g 1s)^2$ and $(\sigma_u 1s)^2$. Similarly, electrons of principal quantum number equal to 2 in the separated atom will give rise to the closed shells $(\sigma_g 2s)^2$, $(\sigma_u 2s)^2$, $(\pi_g 2p)^4$ and $(\pi_u 2p)^4$ in the molecule whose nuclei are widely separated. The numbers of electrons in closed shells are the same as those derived for a molecule with unlike nuclei; the only difference in the representation arises from the fact that in the latter case the electrons do not have the g and u symmetry character, and so they are distinguished by the subscripts A and B. For simplicity this subscript is generally omitted, and the distinction between the orbitals associated with one atom or the other, when the nuclei do not have the same charge, is achieved by marking one with an asterisk, thus $\sigma 1s$ and $\sigma^* 1s$.

Wave mechanical calculations indicate that a σ electron in a g state is more firmly bound than one with the same quantum numbers but with u symmetry; the reverse is true for a π electron, which is more firmly bound in the u state. The order of decreasing binding in a molecule with nuclei of equal charge is thus, in general, $\sigma_g 1s$, $\sigma_u 1s$, $\sigma_g 2s$, $\sigma_u 2s$, $\sigma_g 2p$, $\pi_u 2p$, $\pi_g 2p$, $\sigma_u 2p$; it will be noted that all the $\pi 2p$ electrons are more firmly bound than are those in the $\sigma_u 2p$ orbital. If the nuclei do not carry the same charge, analogous electrons are usually more firmly bound on one atom than on the other; those with the less firm binding are marked with the asterisk, so that the order of binding of the first twenty electrons is approximately $\sigma 1s$, $\sigma^* 1s$, $\sigma 2s$, $\sigma^* 2s$, $\sigma 2p$, $\pi 2p$, $\sigma^* 2p$, $\pi^* 2p$.

It is of interest to compare the orbitals of the first ten electrons in a molecule at small internuclear distances, as derived from the united atom, with those for the same number of electrons when the nuclei are far apart, as deduced from the quantum numbers in the separated atoms. In the first case the orbitals are represented by $(1s\sigma)^2$, $(2s\sigma)^2$, $(2p\sigma)^2$ and $(2p\pi)^4$, while in the latter they are $(\sigma 1s)^2$, $(\sigma^* 1s)^2$, $(\sigma 2s)^2$, $(\sigma^* 2s)^2$ and $(\pi 2p)^4$. It is evident that as the nuclei are drawn apart there must be changes in one or more of the quantum numbers. As will be seen later, there is, in most cases, a definite correlation between the electronic orbitals as the nucleus of the united atom is split up into two nuclei and the distance between them is steadily increased. This correlation is of considerable importance in throwing light on the problems of molecular stability.

41a. Molecular Terms and Electron Orbitals.—By making the usual assumption that the orbital angular momenta of the electrons are strongly coupled among themselves, and that the spins are also strongly coupled together, it is not a difficult matter to evaluate the resultant quantum number for the molecule, provided its electronic configuration is known. It is at this point that the connection between the latter and the term symbol becomes apparent. A knowledge of molecular states, derived from

a study of band spectra, can be used to confirm or to deny a proposed electronic structure.

The quantum number Λ for the component of the resultant orbital angular momentum in the direction of the internuclear axis is obtained by summing the quantum numbers λ for the separate electrons. Algebraic summation is employed since the λ 's are already components along the internuclear axis, but in determining the possible values of Λ it must be remembered that λ can be positive or negative. The process of summation is simplified by taking into consideration the fact that for a closed shell the λ sum is zero, since there are equal numbers of electrons with positive and negative values. It is sufficient, therefore, to restrict attention to the electrons lying outside closed shells. If a molecule has only a single σ or a single π electron of this type, Λ can be only 0 or 1, respectively; the molecule must then be in a Σ or a Π state, respectively. A quantum mechanical treatment shows that the Σ state arising in this manner must have positive symmetry, i.e., it is a Σ^+ state. When the molecule contains one σ , i.e., $\lambda = 0$, and one π , i.e., $\lambda = 1$, electron outside closed shells, the only possible value of Λ is 1; hence a Π state is the result. In the case of one π and one δ electron, the λ values are 1 and 2, respectively; hence Λ can be either 3, i.e., $2 + 1$, or 1, i.e., $2 - 1$, and the possible molecular states are Π and Φ .

The multiplicities of the various states are equal, as usual, to $2S + 1$, where S is the resultant spin quantum number; this is obtained by adding the m_s values for the individual electrons, with due allowance as to the sign. Since m_s is either $+\frac{1}{2}$ or $-\frac{1}{2}$, the resultant spin S for the molecule will be integral if it contains an even number of electrons, and half-integral if the number of electrons is odd. The term multiplicity $2S + 1$ is therefore odd or even, according as the number of electrons in the molecule is even or odd, respectively. Because every closed shell must contain equal numbers of electrons with opposite spins, such shells contribute nothing to the resultant spin. In the evaluation of S it is consequently necessary to consider only electrons outside closed shells. If the molecule consists entirely of closed shells, both Λ and S are zero; these are the characteristics of a $^1\Sigma$ state. It is because most stable diatomic molecules have this type of electronic configuration that they have $^1\Sigma$ ground states, as was tacitly assumed in Chapter IV. For a single electron outside closed shells, whether it be σ , π or δ , the resultant spin is $\frac{1}{2}$, and hence $2S + 1$ is equal to 2; the states corresponding to such electrons are consequently $^2\Sigma^+$, $^2\Pi$ and $^2\Delta$ respectively. For one σ and one π electron, S may be 1, i.e., $+\frac{1}{2} + \frac{1}{2}$, or 0, i.e., $+\frac{1}{2} - \frac{1}{2}$, so that the multiplicity can be 3 and 1. The two states $^3\Pi$ and $^1\Pi$ are thus theoretically possible. It is obvious that two electrons of any kind outside closed shells will give rise to multiplicities of 3 and 1.

41b. Equivalent and Nonequivalent Electrons.—By following the directions given, it is a relatively simple matter to derive the possible molecular term symbols for any reasonable number of electrons outside closed shells. The positive or negative symmetry character of Σ terms is, however, obtained from quantum mechanics. The results, as regards multiplicity and

symmetry character, vary according as the electrons are equivalent or non-equivalent. In the cases already considered it was tacitly assumed that they were nonequivalent, so that there was no restriction concerning the sign of the spin quantum number m , for electrons outside closed shells. If the electrons are equivalent, however, the possible electronic spins, and hence the resultant S , are restricted. This restriction may be illustrated by means of an example. Suppose that, apart from closed shells, the molecule has two π electrons which are not equivalent; Λ may be 2, i.e., $1 + 1$, or 0, i.e., $1 - 1$, and S can be 1 or 0, so that the possible molecular states

TABLE XVI. ELECTRON ORBITALS AND MOLECULAR TERMS

	Nonequivalent Electrons	Equivalent Electrons
$\sigma\sigma$	$^1\Sigma^+, ^3\Sigma^+$	$\sigma^2 \quad ^1\Sigma^+$
$\sigma\pi$	$^1\Pi, ^3\Pi$	
$\sigma\delta$	$^1\Delta, ^3\Delta$	
$\pi\pi$	$^1\Sigma^+, ^3\Sigma^+, ^1\Sigma^-, ^3\Sigma^-, ^1\Delta, ^3\Delta$	$\pi^2 \quad ^1\Sigma^+, ^3\Sigma^-, ^1\Delta$
$\pi\delta$	$^1\Pi, ^3\Pi, ^1\Phi, ^3\Phi$	
$\delta\delta$	$^1\Sigma^+, ^3\Sigma^+, ^1\Sigma^-, ^3\Sigma^-, ^1\Gamma, ^3\Gamma$	$\delta^2 \quad ^1\Sigma^+, ^3\Sigma^-, ^1\Gamma$
$\sigma\sigma\sigma$	$^2\Sigma^+(2), ^4\Sigma^+$	
$\sigma\sigma\pi$	$^2\Pi(2), ^4\Pi$	
$\sigma\pi\pi$	$^2\Sigma^+(2), ^4\Sigma^+(2), ^2\Sigma^-(2), ^4\Sigma^-, ^2\Delta(2), ^4\Delta$	
$\pi\pi\pi$	$^2\Pi(6), ^4\Pi(3), ^2\Phi(2), ^4\Phi$	$\pi^3 \quad ^2\Pi$
Combination of Equivalent and Nonequivalent Electrons		
$\pi^2\sigma$	$^2\Sigma^+, ^2\Sigma^-, ^4\Sigma^-, ^2\Delta$	
$\pi^2\pi$	$^2\Pi(3), ^4\Pi, ^2\Phi$	
$\pi^2\delta$	$^2\Sigma^+, ^2\Sigma^-, ^2\Delta(2), ^4\Delta, ^2\Gamma$	
$\pi^2\pi\sigma$	$^1\Pi(3), ^3\Pi(4), ^5\Pi, ^1\Phi, ^3\Phi$	
$\pi^2\pi^2$	$^1\Sigma^+(3), ^1\Sigma^-, ^3\Sigma^+, ^3\Sigma^-(2), ^5\Sigma^+, ^1\Delta(2), ^3\Delta(2), ^1\Gamma$	
$\pi^3\sigma$	$^1\Pi, ^3\Pi$	
$\pi^3\pi$	$^1\Sigma^+, ^1\Sigma^-, ^3\Sigma^+, ^3\Sigma^-, ^1\Delta, ^3\Delta$	
$\pi^3\delta$	$^1\Pi, ^3\Pi, ^1\Phi, ^3\Phi$	
$\pi^3\pi^2$	$^2\Pi(3), ^4\Pi, ^2\Phi$	
$\pi^3\pi^3$	$^1\Sigma^+, ^1\Sigma^-, ^3\Sigma^+, ^3\Sigma^-, ^1\Delta, ^3\Delta$	

are $^1\Sigma$, $^3\Sigma$, $^1\Delta$ and $^3\Delta$. The Σ states occur with both positive and negative symmetry, so that six states are possible. If the two π electrons are equivalent and λ is $+1$ or -1 for both, then the spins must be opposed (antiparallel) in accordance with the requirements of the Pauli principle. Hence, when Λ is 2, S must be zero, so that $^1\Delta$ is the only permitted state of this type; the $^3\Delta$ state consequently does not occur. If λ is $+1$ for one electron and -1 for the other, so that Λ is zero, i.e., for Σ states, the spins may be either parallel or antiparallel without contravention of the Pauli principle, i.e., S may be 1 or 0. Such states can therefore occur with multiplicities of 3 and 1, although quantum mechanics restricts the former to positive and the latter to negative states, i.e., $^1\Sigma^+$ and $^3\Sigma^-$. As a result of the equivalence of the π electrons, the number of possible molecular terms is reduced from six to three.

If the molecule contains both equivalent and nonequivalent electrons, the restriction as to the values of m , applies to the former but not to the latter. The possible values of Λ and S are then found in the manner already described; the positive and negative characters of Σ states are obtained from quantum mechanics. The results derived for a number of simpler cases are given in Table XVI; an exponent is employed to represent equivalent electrons, e.g., σ^2 , π^3 , etc., whereas the symbols $\sigma\sigma$, $\pi\pi\pi$, etc., imply nonequivalent electrons. A combination of nonequivalent and equivalent electrons is indicated by a symbol such as $\pi^2\sigma$ or $\pi^2\pi$; the latter refers to two equivalent and one nonequivalent π electrons. As mentioned above, single σ , π and δ electrons outside closed shells give $^2\Sigma^+$, $^2\Pi$ and $^2\Delta$ states, respectively; closed shells, i.e., σ^2 , π^4 and δ^4 , always yield $^1\Sigma^+$ states. These simple cases are not included in the tabulation.⁶

If the two nuclei constituting the molecule have equal charges, the states will have the g or u symmetry property. All terms corresponding to a particular electronic configuration will be represented by the same eigenfunction and hence they will all have the same g or u character. If the number of u electrons, e.g., σ_u , π_u , etc., in the molecule is even, the states are g , but if the number is odd then they are all u states.

ELECTRONIC CONFIGURATIONS: HYDROGEN COMPOUNDS⁷

42a. The Hydrogen Molecule.—The results of the preceding sections may be elaborated by means of a few simple illustrations. The hydrogen atom in its normal (ground) state contains a single $1s$ electron, and the term symbol can be shown to be 2S_0 . Suppose two such atoms are brought together to form a hydrogen molecule: what is the electronic configuration of the molecule, and in what state may it be expected to exist? The three lines of approach that have been described may be utilized in an attempt to answer these questions.

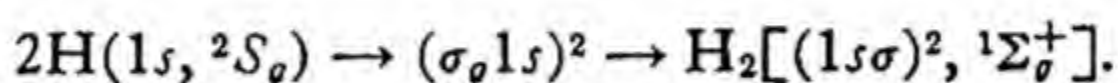
First, reference to Table XV shows that two identical 2S atoms can give rise to $^1\Sigma_0^+$ and $^3\Sigma_0^+$ terms; one of these probably represents the state of the normal hydrogen molecule. Second, if the two hydrogen atoms were brought so close that they coalesced, the resulting united atom would be the helium atom, the lowest state of which has a 1S_0 term. The nucleus of the helium atom is now imagined to be split into two hydrogen nuclei of equal charge; the value of Λ for the resulting molecule can only be zero, since L for the helium atom is zero. The spin and g and u symmetry properties remain unchanged, and so a molecular $^1\Sigma_0^+$ state is obtained. The sum of $L + \sum l$ for the helium atom is zero, and hence the hydrogen molecule must probably be represented by $^1\Sigma_0^+$, this being one of the possible cases predicted by the first method. Third, two electrons may be supposed to be

⁶ Hund, *Z. Physik*, **63**, 719 (1930); Mulliken, ref. 1.

⁷ It should be noted that the configurations given in the following sections are often an approximation, because it may not be possible to represent the actual electronic arrangement in terms of a single structure.

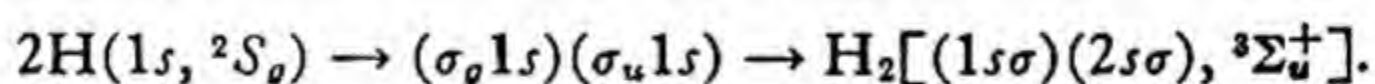
added to a system consisting of two fixed hydrogen nuclei. If the nuclei are far apart, the lowest orbitals may be described by the symbols $\sigma_g 1s$, and if both electrons enter this orbital, the spins must be antiparallel; the resulting configuration will then be $(\sigma_g 1s)^2$. If the nuclei are close together, a better representation for the two electrons would be $(1s\sigma)^2$; in either case, two σ electrons constitute a closed shell and so give a $^1\Sigma^+$ state. Since both electrons have g symmetry, the number of u electrons is zero; as this is an even number, the state of the hydrogen molecule must be $^1\Sigma_g^+$, in agreement with the conclusion reached from the hypothetical splitting of the helium nucleus.

It may be regarded as established, therefore, that the formation of a normal hydrogen molecule from two normal hydrogen atoms may then be written as follows:



The dissociation of the normal hydrogen molecule into hydrogen atoms would be indicated by reversing the representation given above.

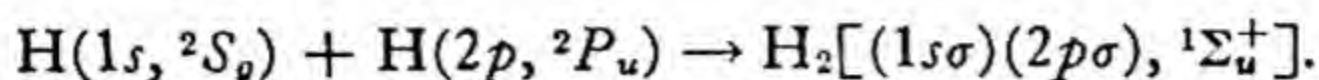
There still remains to be considered the $^3\Sigma_u^+$ state that may be obtained from two 2S_g hydrogen atoms. If one of the electrons enters the lowest orbital, i.e., $\sigma_g 1s$, while the other goes into the slightly higher $\sigma_u 1s$ orbital, the resulting hydrogen molecule, for widely separated nuclei, would be $(\sigma_g 1s)(\sigma_u 1s)$, which would become $(1s\sigma)(2s\sigma)$ as the nuclei came closer together. These configurations both represent two nonequivalent σ electrons, and the resulting states, according to Table XVI, should be $^1\Sigma_u^+$ and $^3\Sigma_u^+$; the u symmetry is derived from the fact that the number of u electrons is odd. The $^3\Sigma_u^+$ state of the hydrogen molecule may thus be derived from two normal hydrogen atoms in the following manner:



For reasons to be explained later, a configuration of this type should be unstable with respect to normal hydrogen atoms; it corresponds, in fact, to the unstable form of molecular hydrogen, with the antisymmetric orbital eigenfunction (parallel spins), foretold theoretically by means of quantum mechanics in Chapter III.

The theoretically possible $^1\Sigma_u^+$ term for the hydrogen molecule, which may arise from the combination of two nonequivalent σ electrons, evidently cannot be derived from two normal atoms, since these give the $^3\Sigma_u^+$ state. It is probable that the $^1\Sigma_u^+$ term is formed from one normal $(1s, ^2S_g)$ and one excited hydrogen atom; the latter atom is likely to be the $2p, ^2P_u$ state. It can be seen from Table XIV that combination of an S_g with a P_u atom can give rise to a Σ^+ state; since the two nuclei have equal charges, this may have either g or u symmetry. If the spins of the two electrons are opposed (antiparallel) then the resultant spin will be zero and the multiplicity of the molecular state will be unity. Hence, the postulated $^1\Sigma_u^+$ state of molecular hydrogen could be produced by the combination of a $1s\sigma$ and a $2p\sigma$ electron,

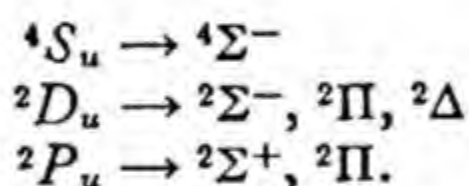
derived from the 2S_g (normal) and 2P_u (excited) atoms, respectively; thus,



Other excited states of the hydrogen molecule can be obtained from the same combination of atoms, but these need not be discussed here. It is of interest to call attention to the fact that the excited $1s2p, ^1P_u$ state of helium, acting as a united atom, can give rise, theoretically, to a $^1\Sigma_u^+$ molecular state of hydrogen, which is probably the same as the one under consideration, as well as to a $^1\Pi_u$ state.

Further discussion of the subject of molecular hydrogen will be deferred until later, when some general rules will be developed which permit an estimate to be made of the relative stabilities of the various molecular states.

42b. Diatomic Hydrides.—The diatomic hydrides, such as BH, CH, NH and OH, as well as LiH, NaH, CaH and AlH, and the more familiar chemically stable HF, HCl, HBr and HI, are of special interest because, apart from molecular hydrogen itself, they are probably the only group of molecules that approach the united atom in structure; this is to be expected from the small size of the hydrogen atom. The CH radical, about which much is known spectroscopically, will be chosen to illustrate the methods used in the study of electronic structures and states of the diatomic hydrides. The united atom corresponding to CH is the nitrogen atom; this has a 4S_u ground state, with 2D_u and 2P_u states having slightly higher energies. As seen in Section 39c, hypothetical division of the nitrogen nucleus should give rise to the following states of the CH molecule:



In considering the arrangement of the electrons in the CH molecule, and in other similar hydrides in which the two nuclei are close together, it is simpler to start with the electronic configuration in the united atom. The three lowest states, i.e., 4S_u , 2D_u and 2P_u , of the nitrogen atom may be represented by the scheme $1s^2 2s^2 2p^3$, and as the atomic electron orbitals pass over into the molecular orbitals of CH, the most stable arrangement would probably be $(1s\sigma)^2(2s\sigma)^2(2p\sigma)^2 2p\pi$. The order of filling up the shells is in accordance with the scheme given previously; the $1s\sigma$ group is most firmly bound, then comes the $2s\sigma$ group, followed by the $2p\sigma$ and then the $2p\pi$ group. It will be remembered, of course, that there can be no more than two σ electrons in each shell. In the proposed configuration there is only one π electron outside closed shells, and so the scheme represents a $^2\Pi$ state.

Another possibility, which could lead to states of higher energy, would be for one of the $2p\sigma$ electrons to become a $2p\pi$ electron, leading to the configuration $(1s\sigma)^2(2s\sigma)^2(2p\sigma)(2p\pi)^2$. There are one σ electron and two equivalent π electrons outside closed shells; this is the arrangement represented by the symbol $\sigma\pi^2$ (or $\pi^2\sigma$) in Table XVI, and according to that table the corre-

sponding molecular terms are $^2\Sigma^+$, $^2\Sigma^-$, $^4\Sigma^-$ and $^2\Delta$. A third possibility to be considered is that the second $2p\sigma$ electron is raised to the $2p\pi$ level, giving $(1s\sigma)^2(2s\sigma)^2(2p\pi)^3$ for the CH molecule. This would mean that there are three equivalent π electrons outside closed shells, and hence the molecule would be in a $^2\Pi$ state (Table XVI). A consideration of the reasonable electronic configurations has thus led to the possibility of six states for the CH molecule which are, in fact, identical with the six derived from the hypothetical splitting of the nucleus of the nitrogen atom. In four of the six cases an exact correlation between the initial state of the nitrogen atom, and the electronic arrangement and state of the CH molecule can be made at once; thus,

Nitrogen Atom	CH Molecule
$1s^2 2s^2 2p^3$, 4S_u	$(1s\sigma)^2(2s\sigma)^2(2p\sigma)(2p\pi)^2$, $^4\Sigma^-$
$1s^2 2s^2 2p^3$, 2D_u	$\left\{ \begin{array}{l} (1s\sigma)^2(2s\sigma)^2(2p\sigma)(2p\pi)^2, \quad ^2\Sigma^- \\ \quad ? \quad \quad \quad ^2\Pi \\ (1s\sigma)^2(2s\sigma)^2(2p\sigma)(2p\pi)^2, \quad ^2\Delta \end{array} \right.$
$1s^2 2s^2 2p^3$, 2P_u	$\left\{ \begin{array}{l} (1s\sigma)^2(2s\sigma)^2(2p\sigma)(2p\pi)^2, \quad ^2\Sigma^+ \\ \quad ? \quad \quad \quad ^2\Pi \end{array} \right.$

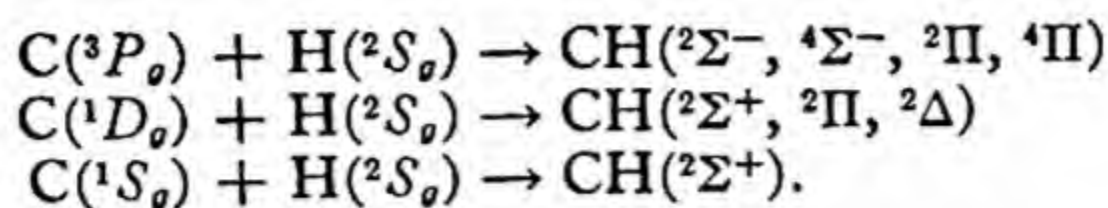
The only doubt is concerned with the assignment of the two $^2\Pi$ states; it is uncertain to which of these states, arising from the 2D_u and the 2P_u states of the nitrogen atom, the alternative configurations $(1s\sigma)^2(2s\sigma)^2(2p\sigma)^2 2p\pi$ and $(1s\sigma)^2(2p\sigma)^2(2p\pi)^3$ should be attributed. Since 2D_u represents a lower energy state of the nitrogen atom than does 2P_u , it is probable that this would give rise to the lower energy state of the molecule CH, and this is undoubtedly the former of the two electronic configurations just given. The correlations are thus:

Nitrogen Atom	CH Molecule
$1s^2 2s^2 2p^3$, 2D_u	$(1s\sigma)^2(2s\sigma)^2(2p\sigma)^2 2p\pi$, $^2\Pi$
$1s^2 2s^2 2p^3$, 2P_u	$(1s\sigma)^2(2s\sigma)^2(2p\pi)^3$, $^2\Pi$

The latter of these two states would probably be unstable with respect to normal carbon and hydrogen atoms, while the other should be, spectroscopically at least, a stable form. It is significant that the experimentally observed $^2\Pi$ state is a regular doublet, that is to say, the level with the smallest value of the quantum number Ω has the lowest energy. This is what is to be expected, according to wave mechanical calculations, for a molecule with one π electron outside closed shells. If there were three such electrons, as in the alternative $^2\Pi$ state, the doublet should theoretically be an inverted one.

The third mode of attack on the problem of the electronic states of the CH molecule, starting from the separated atoms, may now be considered. The most stable electronic configuration of the carbon atom is $1s^2 2s^2 2p^2$, which gives rise to the 3P_o ground state, as well as to 1D_o and 1S_o states with somewhat higher energies. Each of these may be brought, in turn, gradually

closer to a normal 2S_0 hydrogen atom; the possible states of the resulting CH molecule are then found by Table XIV to be as follows:



The three states $^2\Sigma^-$, $^4\Sigma^-$ and $^2\Delta$ may be identified unequivocally with three of the electronic states given previously, but in addition to the uncertainty that existed before in connection with the $^2\Pi$ states, there is now another doubt because there are two possible $^2\Sigma^+$ states. Further, a $^4\Pi$ state has made its appearance. The $^2\Pi$ state arising from the 3P carbon atom will probably represent a lower energy state than that obtained from the 1D atom; hence the former may be identified with the configuration $(1s\sigma)^2(2s\sigma)^2(2p\sigma)^22p\pi$, and the latter with $(1s\sigma)^2(2s\sigma)^2(2p\pi)^3$. Similarly, the $^2\Sigma^+$ state obtained from the 1D carbon atom is probably to be represented by $(1s\sigma)^2(2s\sigma)^2(2p\sigma)(2p\pi)^2$, while the $^2\Sigma^+$ state from the higher energy 1S state of the carbon atom will probably be less stable. A possible configuration for this state of the CH molecule would be $(1s\sigma)^2(2s\sigma)^2(2p\pi)^23s\sigma$ with the electrons $\pi^2\sigma$ outside closed shells; such an arrangement would yield a $^2\Sigma^+$ state, among others (Table XVI).

There still remains the $^4\Pi$ state of CH which may arise from the lowest state (3P) of the carbon atom; the most reasonable structure is $(1s\sigma)^2(2s\sigma)^2(2p\sigma)(2p\pi)3s\sigma$, with $\sigma\pi\sigma$ electrons outside closed shells. Such a configuration would represent an unstable molecule which could be in a $^4\Pi$ state (see $\sigma\sigma\pi$ in Table XVI). The complete correlation scheme for the CH molecule developed above is summarized below. The states marked with an asterisk are expected to be unstable states.

Nitrogen Atom	CH Molecule	C atom	H atom
$1s^22s^22p^3$, $^4S_u \rightarrow$	$(1s\sigma)^2(2s\sigma)^2(2p\sigma)(2p\pi)^2$, $^4\Sigma^-$	$\rightarrow 1s^22s^22p^2$, 3P_0	$+ 1s$, 2S_0
$1s^22s^22p^3$, $^2D_u \rightarrow$	$(1s\sigma)^2(2s\sigma)^2(2p\sigma)(2p\pi)^2$, $^2\Sigma^-$	$\rightarrow 1s^22s^22p^2$, 3P_0	$+ 1s$, 2S_0
	$(1s\sigma)^2(2s\sigma)^2(2p\sigma)^22p\pi$, $^2\Pi$	$\rightarrow 1s^22s^22p^2$, 3P_0	$+ 1s$, 2S_0
	$(1s\sigma)^2(2s\sigma)^2(2p\sigma)(2p\pi)^2$, $^2\Delta$	$\rightarrow 1s^22s^22p^2$, 1D_0	$+ 1s$, 2S_0
$1s^22s^22p^3$, $^2P_u \rightarrow$	$(1s\sigma)^2(2s\sigma)^2(2p\sigma)(2p\pi)^2$, $^2\Sigma^+$	$\rightarrow 1s^22s^22p^2$, 1D_0	$+ 1s$, 2S_0
	$^*(1s\sigma)^2(2s\sigma)^2(2p\pi)^3$, $^2\Pi$	$\rightarrow 1s^22s^22p^2$, 1D_0	$+ 1s$, 2S_0
Excited State \rightarrow	$^*(1s\sigma)^2(2s\sigma)^2(2p\sigma)(2p\pi)3s\sigma$, $^4\Pi$	$\rightarrow 1s^22s^22p^2$, 3P_0	$+ 1s$, 2S_0
Excited State \rightarrow	$^*(1s\sigma)^2(2s\sigma)^2(2p\pi)^23s\sigma$, $^2\Sigma^+$	$\rightarrow 1s^22s^22p^2$, 1S_0	$+ 1s$, 2S_0

42c. Potential Energy Curves.—With the information obtained in Section 42b, it is possible to interpret the potential energy diagram of the CH molecule depicted in Fig. 31; the full curves are for spectroscopically observed states, whereas the dashed curves represent postulated states. The $^2\Pi$ state with the electronic configuration, $(1s\sigma)^2(2s\sigma)^2(2p\sigma)^22p\pi$, dissociating to give a normal (3P) carbon atom, is undoubtedly the most stable form of CH; it should have, as the diagram shows, the deepest potential energy curve. Of the states corresponding to the next stable configuration,

$(1s\sigma)^2(2s\sigma)^2(2p\sigma)(2p\pi)^2$, the $^4\Sigma^-$ should be the lowest; first, because it has the largest multiplicity and, second, because it is correlated with the lowest energy (4S) state of the united atom, nitrogen. The $^4\Sigma^-$ state also dissociates to give a normal carbon atom, and hence its potential energy curve may be

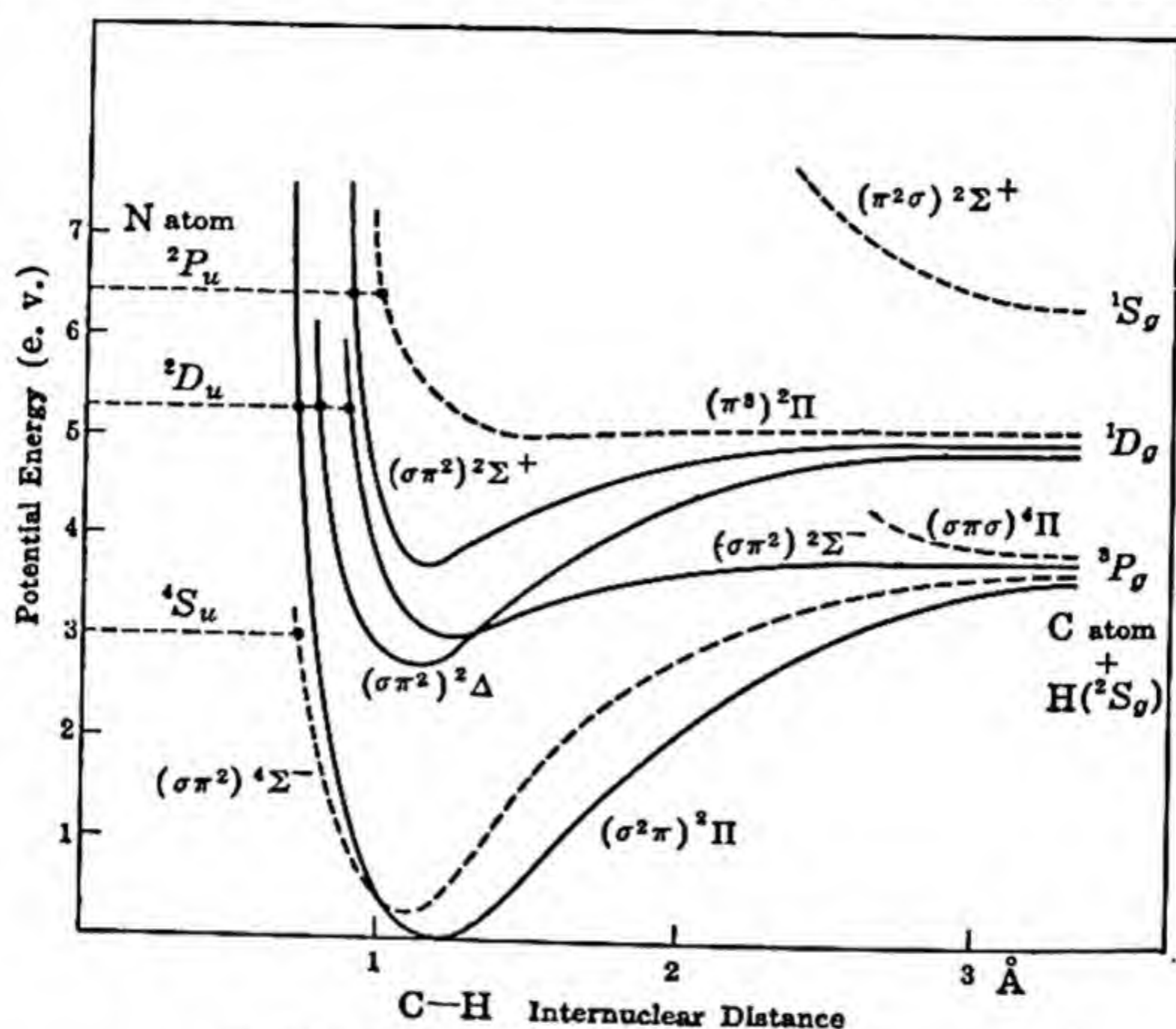


FIG. 31. Potential energy curves of CH molecule

expected to be as shown by the lowest dashed line. Of the other three states of the CH molecule corresponding to the same electronic configuration, the $^2\Delta$ and $^2\Sigma^-$ are both correlated with the same (2D) state of the nitrogen atom; hence the potential energies at the equilibrium distances will not be very different, although the $^2\Delta$ state would perhaps be the lower of the two because of the greater Λ value. The $^2\Sigma^-$ state, as shown in the summary given above, dissociates to yield a normal (3P) carbon atom, while the $^2\Delta$ state produces a 1D carbon atom. The fourth ($^2\Sigma^+$) state for the same configuration also yields a 1D carbon atom, but as the state of the CH molecule is correlated with a higher energy (2P) state of the united (nitrogen) atom, its potential energy curve will be less deep than that of the $^2\Delta$ and $^2\Sigma^-$ states.

There still remain the three postulated states, viz.,

$(1s\sigma)^2(2s\sigma)^2(2p\sigma)(2p\pi)3s\sigma$, $^4\Pi$; $(1s\sigma)^2(2s\sigma)^2(2p\pi)^23s\sigma$, $^2\Sigma^+$;

and $(1s\sigma)^2(2s\sigma)^2(2p\pi)^3$, $^2\Pi$;

in view of the raising of electrons to higher energy levels, none of these states would be expected to have any appreciable stability. However, since the

$^2\Pi$ state of CH which gives a 1D carbon atom on dissociation is correlated with the united atom, nitrogen, in the 2P state, this may have slight stability, as is indicated by the long horizontal portion of the postulated potential energy curve. The other two states, $^4\Pi$ and $^2\Sigma^+$, can be correlated only with highly energetic states of the nitrogen atom; these forms of the CH molecule may thus be expected to be repulsive at all internuclear distances.

42d. The Hydrogen Halides.—The treatment applied to the CH molecule can be adapted to the consideration of other hydrides, although there are generally fewer possible states. Since the halogen hydrides are compounds of special interest, the structure of hydrogen fluoride will be discussed briefly; the results for the other halogen hydrides are quite analogous. The united atom corresponding to hydrogen fluoride is neon, and this, like all the inert gases of Group 0, consists entirely of closed shells, viz., $1s^2 2s^2 2p^6$, and has a 1S_0 ground term. Splitting of the neon nucleus into the nuclei of hydrogen and fluorine should result in the formation of a $^1\Sigma^+$ state only. Further, the electronic structure of the neon atom, just given, would be correlated with the most stable arrangement, i.e., $(1s\sigma)^2(2s\sigma)^2(2p\sigma)^2(2p\pi)^4$, of hydrogen fluoride; the latter is made up of closed shells only, and so constitutes a $^1\Sigma^+$ state. Finally, by bringing together a 2S_0 hydrogen atom and a 2P_u (normal) fluorine atom, the resulting molecular states, from Table XIV, would be $^1\Sigma^+$, $^3\Sigma^+$, $^1\Pi$ and $^3\Pi$. The $^1\Sigma^+$ state may be immediately identified with the molecule of hydrogen fluoride derived from the normal united atom neon, and having the configuration represented above. The $^1\Pi$ and $^3\Pi$ states, which may arise from normal hydrogen and fluorine atoms, evidently refer to the excited electronic configuration $(1s\sigma)^2(2s\sigma)^2(2p\sigma)^2(2p\pi)^3 3s\sigma$ in which one of the $2p\pi$ electrons has been raised to the $3s\sigma$ level. Reference to Table XVI shows that the group $\pi^3\sigma$ outside closed shells yields just these states, $^1\Pi$ and $^3\Pi$.

The configuration of the $^3\Sigma^+$ state is not known definitely, but it might well be $(1s\sigma)^2(2s\sigma)^2(2p\sigma)(2p\pi)^4 3s\sigma$, since two nonequivalent σ electrons could give rise to such a state. In view of the fact that this differs from the most stable state by a $2p\sigma$ electron being raised to a $3s\sigma$ level, it would probably be very unstable. The correlations for hydrogen fluoride may thus be represented by the following scheme:

Neon Atom	HF Molecule	H atom	F atom
$1s^2 2s^2 2p^6, ^1S_0 \rightarrow$	$(1s\sigma)^2(2s\sigma)^2(2p\sigma)^2(2p\pi)^4, ^1\Sigma^+$	$\rightarrow 1s, ^2S_0$	$+ 1s^2 2s^2 2p^6, ^2P_u$
Excited states \rightarrow	$^*(1s\sigma)^2(2s\sigma)^2(2p\sigma)^2(2p\pi)^3 3s\sigma, ^1\Pi$	$\rightarrow 1s, ^2S_0$	$+ 1s^2 2s^2 2p^6, ^2P_u$
	$(1s\sigma)^2(2s\sigma)^2(2p\sigma)^2(2p\pi)^3 3s\sigma, ^3\Pi$	$\rightarrow 1s, ^2S_0$	$+ 1s^2 2s^2 2p^6, ^2P_u$
	$^*(1s\sigma)^2(2s\sigma)^2(2p\sigma)(2p\pi)^4 3s\sigma, ^3\Sigma^+$	$\rightarrow 1s, ^2S_0$	$+ 1s^2 2s^2 2p^6, ^2P_u$

* Probably unstable.

The behavior of the other halogen hydrides would be quite similar, the essential difference lying in the additional completed shells and the changes in the principal quantum numbers; thus, the normal ($^1\Sigma^+$) state of hydrogen chloride would be $(1s\sigma)^2(2s\sigma)^2(2p\sigma)^2(2p\pi)^4(3s\sigma)^2(3p\sigma)^2(3p\pi)^4$. The electrons

in the shells with principal quantum number 1 and 2, i.e., the *K* and *L* shells, are firmly bound and play little or no part in the formation of the hydrogen chloride molecule. The representation of the electronic configuration is therefore simplified by writing $KL(3s\sigma)^2(3p\sigma)^2(3p\pi)^4$, instead of that given above. Similarly, the $^1\Sigma^+$ ground state of hydrogen bromide would be $KLM(4s\sigma)^2(4p\sigma)^2(4p\pi)^4$.

It is of interest to note that the electronic spectra of the hydrogen halides are continuous, showing no vibrational or rotational structure. This means that the upper combining state is an unstable, repulsive state at all internuclear distances. Since the normal $^1\Sigma$ state would probably combine with the $^1\Pi$ state (cf. Section 31f), it follows that the latter is unstable, as would be expected. The $^3\Pi$ state might be somewhat more stable, but the $^3\Sigma$ state would evidently be very unstable.

ELECTRONIC CONFIGURATIONS: DIATOMIC MOLECULES ⁸

43a. Symbols for Electron Orbitals.—For diatomic molecules other than hydrides, the nuclei are too far apart for the electronic configurations to approximate to that of the united atom. At the same time, the internuclear distance is not sufficiently great for the condition to approach that of the separated atoms, except perhaps for the most firmly bound electrons, namely $(\sigma_g 1s)^2$ and $(\sigma_u 1s)^2$, or $(\sigma 1s)^2$ and $(\sigma^* 1s)^2$, for molecules with equally charged or unequally charged nuclei, respectively. Under these conditions the quantum numbers *n* and *l* of the separated atoms, as represented by such symbols as $2s$, $2p$, $3s$, $3p$, $3d$, etc., frequently do not have any definite significance in the molecule, while those of the united atom have not been attained. For cases of this kind the use of the letters *z*, *y*, *x*, *w*, *v*, ..., has been proposed; these precede the symbols σ , π , δ , ..., to distinguish between different kinds of σ , π , δ , ..., electrons. Although the letters have no precise theoretical significance, they may be regarded as being equivalent to the two quantum numbers which are described by *n* and *l* in the atom. The greater the binding energy of the electrons the closer is the letter to the end of the alphabet; thus a *z* electron would, in general, be more firmly bound than a *y* electron, and a *y* would be more firmly bound than an *x* electron, and so on.

From a study of the excitation energies of a number of simple molecules, it appears that various σ and π orbitals may be arranged in order of increasing binding, at equilibrium values of the internuclear separation, as follows:

$$z\sigma, y\sigma, x\sigma, w\pi, v\pi, u\sigma, \quad \text{or} \quad z\sigma, y\sigma, w\pi, x\sigma, v\pi, u\sigma.$$

The order is approximate and may show slight variations from one molecule to another. Since each letter, *z*, *y*, *x*, etc., is equivalent to two quantum numbers, the restrictions already derived, concerning the numbers of σ , π , δ , etc., electrons in complete shells, still hold. Two σ electrons of the same

⁸ Mulliken, ref. 1.

kind, e.g., $(z\sigma)^2$, $(y\sigma)^2$, $(x\sigma)^2$, constitute a closed shell, and so also do four equivalent π electrons, e.g., $(w\pi)^4$, $(v\pi)^4$.

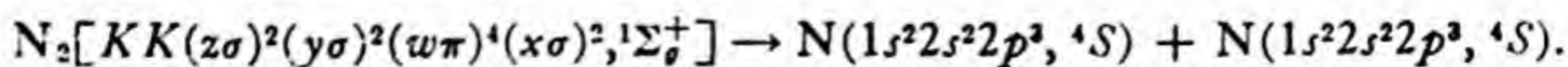
It may be noted that as a general rule, with the exception of hydrogen and helium, the quantum numbers n and l retain their significance in compounds for electrons in the first quantum ($n = 1$) level, i.e., in the K shell. The electrons generally play no part in molecule formation, and so are often referred to as *nonbonding electrons* (cf. Section 45b). The two $1s$ electrons associated with each atom behave in the molecule, for all practical purposes, as if they were unchanged $1s$ electrons, or K electrons, of the respective atoms. For this reason these four firmly bound electrons are generally represented by the symbol KK . It should be remembered that this refers to *four* electrons, viz., $(\sigma_0 1s)^2(\sigma_u 1s)^2$ or $(\sigma 1s)^2(\sigma^* 1s)^2$, each atom having two $1s$ (nonbonding) electrons, with antiparallel spins. With elements of high atomic number, it is probable that in addition to the $1s$ electrons, the two $2s$ and six $2p$ electrons are firmly bound to each atom; the group of nonbonding electrons would then be represented by the letters $KKLL$. It must be emphasized, again, that these considerations do not apply for molecules containing hydrogen atoms.

43b. Electronic Configuration of Diatomic Molecules.—In the treatment of diatomic molecules involving atoms other than hydrogen and helium, the most useful mode of attack is to imagine the electrons added one by one to the system of fixed nuclei. Consider, for example, the nitrogen molecule, which has fourteen electrons. This molecule will, most probably, approach the separated atoms in behavior, although the nuclei may perhaps be too far apart for quantum numbers such as $2s$, $2p$, etc., to have any significance. The first four electrons will probably enter the K shells ($n = 1$) of the two nitrogen atoms, and the remaining ten electrons will fill successively the $z\sigma$, $y\sigma$, $x\sigma$ and $w\pi$ levels, in the order given. The electronic configuration of the nitrogen molecule in its ground state might thus be

$$KK(z\sigma)^2(y\sigma)^2(x\sigma)^2(w\pi)^4 \quad \text{or} \quad KK(z\sigma)^2(y\sigma)^2(w\pi)^4(x\sigma)^2.$$

It will be shown from a consideration of the N_2^+ ion that the latter of these alternatives is expected to be the correct one; the $x\sigma$ electrons are probably less firmly bound in this case than are the $w\pi$ electrons. Since all the electron shells are filled and the nitrogen molecule consists of two nuclei with equal charges, it should be in a ${}^1\Sigma_g^+$ state, in either case. This has actually been found spectroscopically to be the state of the normal nitrogen molecule.

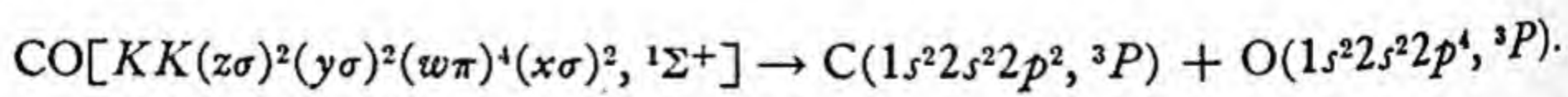
The electronic configuration proposed is undoubtedly the most stable possible for the fourteen electrons, and hence the dissociation of the ${}^1\Sigma_g^+$ molecule should lead to two normal (4S) nitrogen atoms. This suggestion cannot be proved definitely by theoretical reasoning, but some support for it is to be found in Table XV, which shows that two identical 4S atoms can yield a ${}^1\Sigma_g^+$ state, among others. It is thus possible to write for the dissociation of the normal nitrogen molecule,



It may be mentioned that no useful information is obtained by carrying out a hypothetical scission of the united atom, which in this case is the silicon atom; the ground term of the latter is 3P , and so it should give rise to a nitrogen molecule in a triplet state. In view of the fact that there are many more orbitals, corresponding to a given value of the principal quantum number, available in a molecule whose nuclei are relatively far apart, there is not necessarily a direct correlation between the molecule and the united atom in their respective ground states. A correlation between the molecule and the separated atoms is much more likely to exist, and this has been found to be so in the case under discussion.

Although the $z\sigma$ and $y\sigma$ electrons are probably firmly bound in the nitrogen molecule, those in the $x\sigma$ and $w\pi$ orbitals are less strongly held, and excited states of the molecule would result from the transfer of an electron from these shells to the $v\pi$ or $u\sigma$ shells. The states of such excited molecules could be worked out, if required, and correlated, as far as possible, with two nitrogen atoms in their normal or excited states. However, the information on the subject is so confusing that consideration of excited states may better be left to other cases to be treated shortly.

43c. The Structures of Isosteres.—The similarity in physical properties between molecular nitrogen and carbon monoxide is implied in the use of the term *isosteres* to indicate analogous electronic structures based on the electron octet theory of valence. The resemblance between these molecules extends to their spectra, the ground term of carbon monoxide being $^1\Sigma^+$; the g and u symmetry property does not apply here, of course, since the nuclei have different charges. Like the molecule of nitrogen, that of carbon monoxide contains fourteen electrons; hence the electronic structure of the ground state should be identical with that given above for the nitrogen molecule. This similarity between the nitrogen and carbon monoxide molecules is all the more striking because the former results from two identical 4S atoms, while the latter, if it dissociates into normal carbon and oxygen atoms, which is probable, arises from two 3P atoms carrying different nuclear charges. However, $^1\Sigma^+$ is only one of the many states that can arise from the combination of two unlike 3P atoms (cf. Table XIV). The correlation between carbon monoxide and its dissociation products may thus be written



The similarity of the ground terms of nitrogen and carbon monoxide, in spite of the difference in the states of the atoms from which they originate, or into which they dissociate, indicates that the essential factor in determining the structure of the ground state of the molecule is the total number of available electrons. That this is true, at least for diatomic molecules with atoms that are not very dissimilar, will be seen shortly when other cases are considered.

The lowest known state of the singly charged nitrogen molecule-ion N_2^+ , which contains one electron less than the nitrogen molecule, is $^2\Sigma_g^+$, and this is probably the ground state. The observed term $^2\Sigma_g^+$ can be accounted for by the presence of a single σ electron outside closed shells. In the formation of the $^2\Sigma_g^+$ ground state of N_2^+ from the $^1\Sigma_g^+$ ground state of N_2 , the least firmly bound electron of the latter is presumably removed; this must evidently be a σ electron, so as to leave one such electron remaining outside closed shells. It is for this reason that the $x\sigma$ electrons in molecular nitrogen are considered to be less firmly bound than those in the $w\pi$ shell. If the reverse were true, the formation of the N_2^+ ion would probably result from the loss of a $w\pi$ electron, leaving $(w\pi)^3$ outside closed shells; three equivalent π electrons, however, cannot give rise to a Σ state (cf. Table XVI).

The diatomic systems BO, CO^+ and CN, like N_2^+ , have thirteen electrons and their ground states are also $^2\Sigma^+$, there being, of course, no g character since the nuclei carry different charges. It appears, therefore, that the electronic structures of the known lowest states of the isoelectronic systems BO, CO^+ , CN and N_2^+ are identical; thus,

$$KK(z\sigma)^2(y\sigma)^2(w\pi)^4x\sigma, ^2\Sigma^+.$$

For BO, CO^+ and CN, but not for N_2^+ , the second lowest state is $^2\Pi$; this can be accounted for by three equivalent π electrons, in addition to the closed shells. A reasonable structure for this state is then

$$KK(z\sigma)^2(y\sigma)^2(w\pi)^3(x\sigma)^2, ^2\Pi.$$

In this case an electron has presumably been removed from the somewhat more firmly bound $w\pi$ group, rather than from the less strongly held $x\sigma$ shell, thus leading to a higher energy state. It is somewhat unexpected to find that no $^2\Pi$ state has been observed for N_2^+ . It is surmised that this state does exist, but it has not been detected because its energy is very close to that of the slightly lower $^2\Sigma_g^+$ state. This would mean that in the nitrogen molecule the $w\pi$ and $x\sigma$ electrons are almost equally firmly bound, as might have been expected. It is of interest to record that at their equilibrium distances the energies of the $^2\Pi$ and $^2\Sigma$ states become closer in the order BO, CO^+ , CN, so that they might well be almost identical for N_2^+ .

All the members of the group under consideration, i.e., BO, CO^+ , CN and N_2^+ exhibit a still higher $^2\Sigma^+$ state; for the ion N_2^+ , with two identical nuclei, this is a $^2\Sigma_u^+$ state. As in the ground state, this could arise from a single σ electron, apart from closed shells; however, this electron is obviously in different groups in the two $^2\Sigma$ states, and the most probable structure for the higher of these states, which is the second known excited state, is

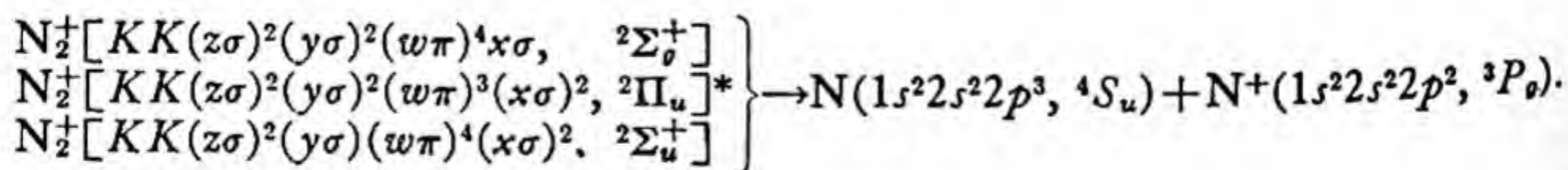
$$KK(z\sigma)^2(y\sigma)(w\pi)^4(x\sigma)^2, ^2\Pi,$$

with the single σ electron in the $y\sigma$ shell. In the case of N_2^+ , this particular excited state would be formed from the nitrogen molecule by the removal of

a relatively firmly held $y\sigma$ electron. That it comes from the $y\sigma$ rather than from the $z\sigma$ group is supported by the fact that the state is ${}^2\Sigma_u^+$, which means that a u electron has been removed from the ${}^1\Sigma_g^+$ nitrogen molecule; of the two types of σ electrons, the less firmly bound, i.e., $y\sigma$, would be the only ones with the u property.

DISSOCIATION PRODUCTS

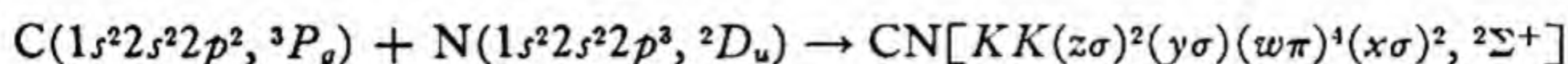
44a. Dissociation of Diatomic Molecules.—It will be apparent from what has been said in connection with the dissociation of $N_2({}^1\Sigma_g^+)$ into $N({}^4S) + N({}^4S)$, and of $CO({}^1\Sigma^+)$ into $C({}^3P) + O({}^3P)$, that in spite of the similarities in the various states of isoelectronic molecules, the correlation between the molecular and atomic states may be very different. This fact is brought out clearly by a comparison of the dissociation of N_2^+ and CN. The nitrogen atom, with the configuration $1s^2 2s^2 2p^3$ has, as seen previously, three low-lying energy states, viz., 4S_u , 2D_u and 2P_u ; corresponding to these there will be three states for the nitrogen atom-ion, N^+ , i.e., $1s^2 2s^2 2p^2$, whose term symbols are 3P_g , 1D_g and 1S_g , analogous to the three states of the carbon atom with the same electronic configuration. The number of possible molecular states of the nitrogen molecule-ion N_2^+ formed by the combination of these atomic states is very large. It is probable, however, that the lower energy states of N_2^+ will be derived from the lowest atomic states which are theoretically capable of yielding molecular states having the appropriate characteristics. Combination of the lowest atomic nitrogen state (4S_u) with the lowest state of the nitrogen atom-ion (3P_g) can give twelve molecular states, namely ${}^6\Sigma^+$, ${}^4\Sigma^+$, ${}^2\Sigma^+$, ${}^6\Pi$, ${}^4\Pi$ and ${}^2\Pi$, each in both g and u states, since the nuclei of N_2^+ are equally charged. It is evident, therefore, that the two observed states of the nitrogen molecule-ion, viz., ${}^2\Sigma_g^+$ and ${}^2\Sigma_u^+$, as well as the predicted ${}^2\Pi_u$, lying between them, can be derived theoretically, and probably are derived, in fact, from a normal nitrogen atom and a normal nitrogen atom-ion, in their lowest energy states. This conclusion may be represented by the following scheme:



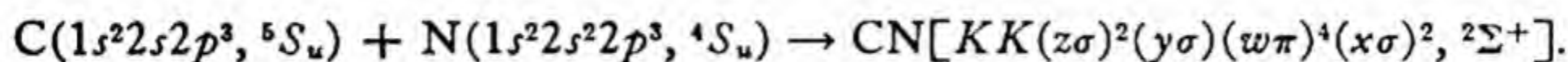
* Unknown state.

Turning now to CN, there are three analogous states; these are in order of increasing energy ${}^2\Sigma^+$, ${}^2\Pi$ and ${}^2\Sigma^+$. From the lowest state of the carbon atom, viz., $1s^2 2s^2 2p^2$, 3P_g , and the lowest state of the nitrogen atom, $1s^2 2s^2 2p^3$, 4S_u , six molecular states can be obtained. One of these is a ${}^2\Sigma^+$ and another is a ${}^2\Pi$ state, which may in all probability be correlated with the two lowest observed states of the CN molecule. However, whereas with N_2^+ , two ${}^2\Sigma^+$ states are possible, one g and one u , there is only one such state for CN, since the two nuclei do not carry equal charges. The upper ${}^2\Sigma^+$ state of CN cannot, therefore, be correlated with two atoms in their ground states,

and hence one of these must be in a somewhat higher energy state. There are two possibilities in this connection; either the carbon atom remains in the 3P_o state and the nitrogen atom is raised to 2D_u , or the carbon atom is excited to 5S_u while the nitrogen remains in the 4S_u state. Either of these combinations can give rise to a $^2\Sigma^+$ molecular state, but it is difficult to make an exact decision between the two possibilities. Utilizing the configuration of the upper $^2\Sigma^+$ state derived above, the two alternative correlations may be written out in the following form:



or



In the first case there are four $2s$ electrons in the separated atoms which are correlated with the three electrons $(z\sigma)^2(y\sigma)$ in the molecule; in the second case, however, there are only three $2s$ electrons to be correlated with the three σ electrons in the CN molecule. From this point of view the second alternative is to be preferred; nevertheless, the argument is not convincing, for at relatively large internuclear distances the difference in binding energy of $x\sigma$ and $y\sigma$ electrons is not great. It is not impossible, therefore, that as the carbon and nitrogen atoms approach, one of the $2s$ atomic electrons goes over into a $x\sigma$ orbital. The essential point to be noted, at the moment, is that whereas the $^2\Sigma_g^+$, $(^2\Pi_u)$ and $^2\Sigma_u^+$ states of the nitrogen molecule-ion N_2^+ may probably, all three, be correlated with the same normal atomic states, this is not true for the isoelectronic molecule CN; for the latter, the two lower states are correlated with the same atomic state, but the upper $^2\Sigma^+$ state must be connected with one normal and one excited atom. The potential energy curves for N_2^+ and CN, which summarize the foregoing discussion, are given in Fig. 32.

Like CN and N_2^+ , the isoelectronic systems NO and O_2^+ possess analogous electronic states, but exhibit differences in the correlations with the respective atomic states on dissociation. As in the case just considered, the two nuclei of O_2^+ are identical, and so combination of a normal oxygen atom with a normal oxygen atom-ion can give two molecular $^2\Pi$ states of O_2^+ , one with

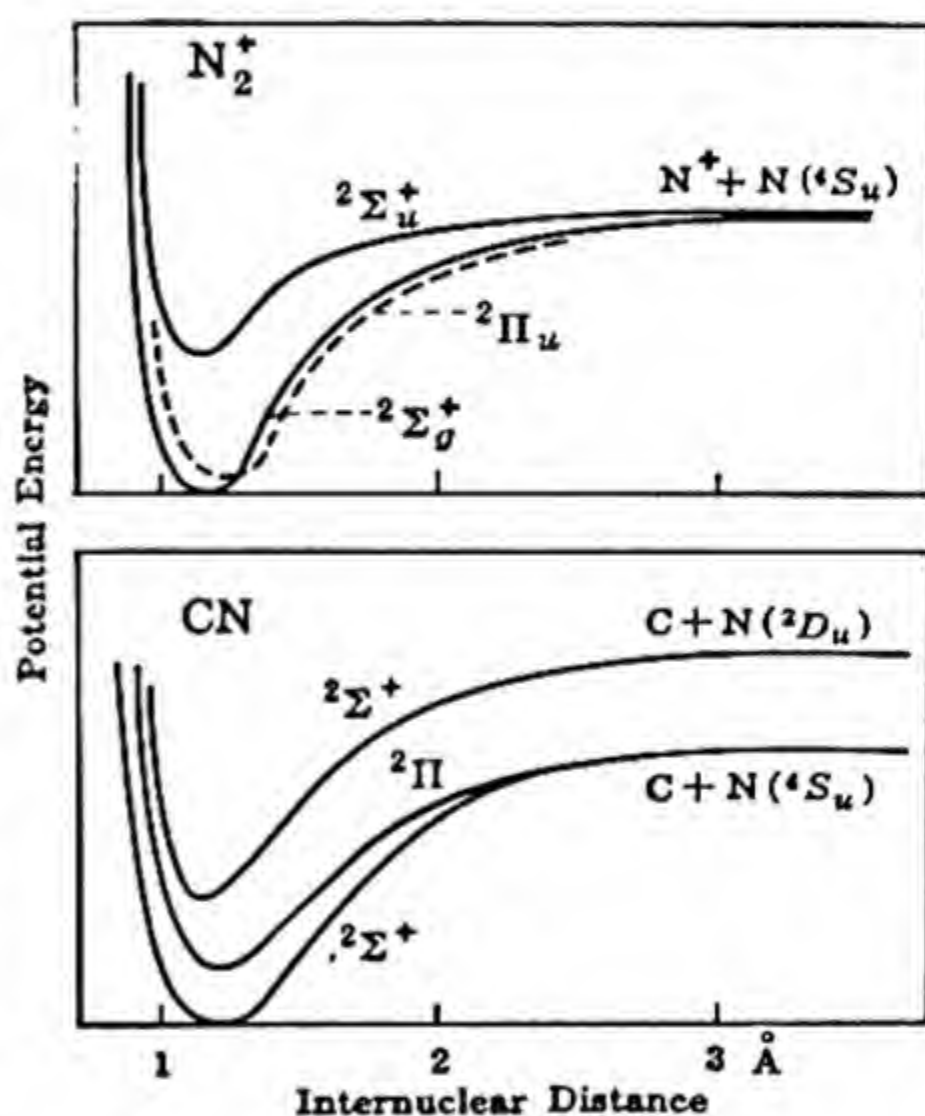


FIG. 32. Potential energy curves for N_2^+ and CN

g and the other with u symmetry. The combination of normal oxygen and normal nitrogen atoms, however, can give only one ${}^2\Pi$ state, since the nuclei are now different. The upper observed ${}^2\Pi$ state of nitric oxide must therefore dissociate into one normal atom and one in a somewhat higher energy state; the latter is probably the 2D nitrogen atom, for $N({}^2D)$ and $O({}^3P)$ represent the lowest pair of atoms capable of giving a second ${}^2\Pi$ state of nitric oxide.

44b. The Oxygen Molecule.—The oxygen molecule has two electrons more than the nitrogen molecule, and these will presumably enter the next shell, i.e., $v\pi$, so that plausible structures of the molecule would be

$$KK(z\sigma)^2(y\sigma)^2(x\sigma)^2(w\pi)^4(v\pi)^2 \quad \text{or} \quad KK(z\sigma)^2(y\sigma)^2(w\pi)^4(x\sigma)^2(v\pi)^2.$$

The only difference between these alternatives is in the interchange of the relative positions of the $w\pi$ and $x\sigma$ groups; in contradistinction to what was observed with the nitrogen molecule, it appears that for the oxygen molecule the former configuration is to be preferred. In either case, the electronic state of the oxygen molecule would be determined by two equivalent $v\pi$ electrons, all the others being in closed shells. According to Table XVI, two such electrons should give rise to the states ${}^1\Sigma^+$, ${}^3\Sigma^-$ and ${}^1\Delta$; since the proposed configuration would involve an even number of u electrons, these states should all have g symmetry. The choice between the three possibilities is facilitated by two considerations; first, the state of highest multiplicity, i.e., ${}^3\Sigma_g^-$, is probably the lowest energy state and hence represents normal molecular oxygen. In the second place, the fact that the normal oxygen molecule is paramagnetic means that the resultant spin vector of the whole molecule is not zero. The closed groups cannot contribute to the spin, and so it is at once evident that the two $v\pi$ electrons must have parallel spins; the resultant spin quantum number is thus unity, i.e., $+\frac{1}{2} + \frac{1}{2}$, and the multiplicity of the normal state of the oxygen molecule must be three. It follows, therefore, that the proposed configurations lead to a ${}^3\Sigma_g^-$ ground state for molecular oxygen, and this is actually the case. The other two states, ${}^1\Delta_g$ and ${}^1\Sigma_g^+$, arising from the same electronic configuration, are also known; they occur in the order given, with energies slightly above that of the ${}^3\Sigma_g^-$ state.

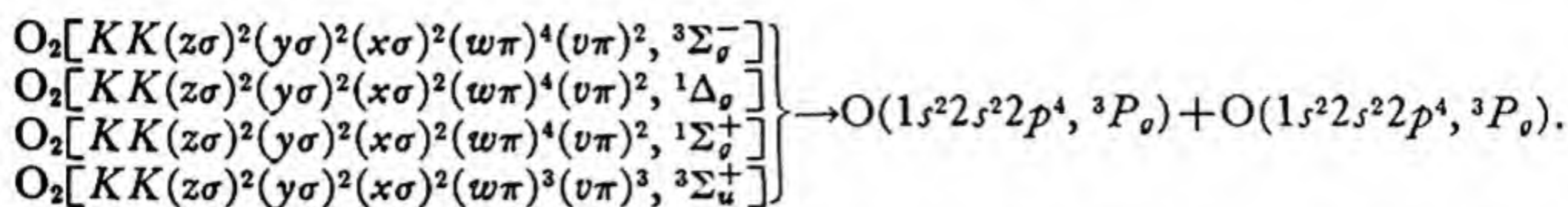
In addition to the three low-lying states just mentioned, there is a much higher ${}^3\Sigma_u^-$ excited state of the oxygen molecule. A reasonable structure for a level of this type would be

$$KK(z\sigma)^2(y\sigma)^2(x\sigma)^2(w\pi)^3(v\pi)^3, {}^3\Sigma_u^-,$$

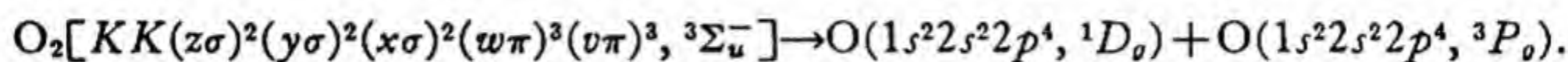
one of the $w\pi$ electrons being raised to the $v\pi$ level. Five other states could arise from this same configuration, i.e., $\pi^3\pi^3$, outside closed shells, but most of these are probably unstable states, with the possible exception of a ${}^3\Sigma_u^+$ state to which reference will be made below.

Two normal oxygen atoms, $1s^2 2s^2 2p^4, {}^3P_o$, are capable of yielding eighteen molecular states (cf. Table XV), among them being ${}^3\Sigma_g^-$, ${}^1\Delta_g$ and ${}^1\Sigma_g^+$, which

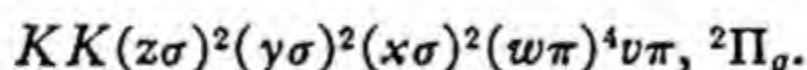
are the three lowest states of the normal oxygen molecule, and also the ${}^3\Sigma_u^+$ excited state, mentioned at the end of the preceding paragraph. It is probable, therefore, that all these molecular states give normal 3P_g atoms on dissociation; thus,



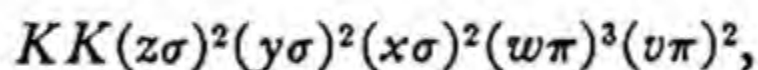
The other excited state, ${}^3\Sigma_u^-$, corresponding to the same electronic configuration as the ${}^3\Sigma_u^+$ state, cannot, however, be derived from two 3P_g atoms. By raising the energy of one of the oxygen atoms to the slightly higher, metastable 1D_g state, a molecular ${}^3\Sigma_u^-$ state becomes possible (cf. Table XIV). A reasonable correlation is therefore



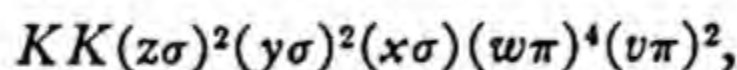
44c. The Oxygen Molecule-Ion.—The lowest state of the oxygen molecule-ion O_2^+ is a regular ${}^2\Pi_g$ term, and this would result from a single π electron apart from closed shells. The loss of one relatively loosely held $v\pi$ electron from a normal oxygen molecule would provide such a configuration for O_2^+ , viz.,



On the other hand, if one of the $w\pi$ electrons is removed from the oxygen molecule, thus,



the states ${}^2\Pi_u(3)$, ${}^4\Pi_u$ and ${}^2\Phi_u$ of excited O_2^+ could result, since the electrons outside closed shells are $\pi^3\pi^2$ (cf. Table XVI). One of the three ${}^2\Pi_u$ states is known, but the others have not been detected. A third type of configuration for O_2^+ , leading to higher energy states, would be



and the three electrons $\sigma\pi^2$ outside closed shells could lead to ${}^2\Sigma_g^+$, ${}^2\Sigma_g^-$, ${}^4\Sigma_g^-$ and ${}^2\Delta_g$ molecular terms. None of these states is known with certainty, but it has been suggested that the bands appearing in the visible spectrum of the oxygen molecule-ion may be due to the transition ${}^4\Sigma_g^- \rightarrow {}^4\Pi_u$, the latter being derived from the $\pi^3\pi^2$ electronic configuration.

The lowest state of the oxygen atom-ion O^+ , $1s^2 2s^2 2p^3$, will probably be 4S_u , like the nitrogen atom, and combination of this with a normal oxygen atom, 3P_g , should yield twelve molecular states, among them being the observed ${}^2\Pi_g$ and ${}^2\Pi_u$ states, mentioned above, and also the possible ${}^4\Pi_u$ state. The ${}^4\Sigma_g^-$ term, however, could not arise from this combination, but it would be one of the states resulting from the union of a normal oxygen atom-ion $O^+({}^4S_u)$ with an oxygen atom in the metastable 1D_g state. The

dissociation correlations of the various states of the oxygen molecule-ion may thus be represented as follows:

$$\left. \begin{aligned} O_2^+ [KK(z\sigma)^2(y\sigma)^2(x\sigma)^2(w\pi)^4v\pi, {}^2\Pi_g] \\ O_2^+ [KK(z\sigma)^2(y\sigma)^2(x\sigma)^2(w\pi)^3(v\pi)^2, {}^4\Pi_u]^* \\ O_2^+ [KK(z\sigma)^2(y\sigma)^2(x\sigma)^2(w\pi)^3(v\pi)^2, {}^2\Pi_u] \end{aligned} \right\} \rightarrow O^+(1s^2 2s^2 2p^3, {}^4S_u) + O(1s^2 2s^2 2p^4, {}^3P_g)$$

$$O_2^+ [KK(z\sigma)^2(y\sigma)^2(x\sigma)(w\pi)^4(v\pi)^2, {}^4\Sigma_g^-]^* \rightarrow O^+(1s^2 2s^2 2p^3, {}^4S_u) + O(1s^2 2s^2 2p^4, {}^1D_g)$$

* Unknown states.

44d. Structures of Other Diatomic Molecules.—The addition of two more electrons to the configuration of the oxygen molecule should yield that of the normal fluorine molecule; it is to be expected that these electrons will complete the $v\pi$ shell; thus

$$F_2 [KK(z\sigma)^2(y\sigma)^2(x\sigma)^2(w\pi)^4(v\pi)^4, {}^1\Sigma_g^+].$$

With all the shells complete, and an even number of u electrons, the state should be ${}^1\Sigma_g^+$, in agreement with observations on the ground state of halogen molecules in general. The normal fluorine atom is in a 4P state, and combination of two such identical atoms will give a ${}^1\Sigma_g^+$ molecular state, in addition to others.

If twenty electrons were added to a system of two neon nuclei, the resulting electronic configuration

$$KK(z\sigma)^2(y\sigma)^2(x\sigma)^2(w\pi)^4(v\pi)^4(u\sigma)^2$$

should represent the structure of the Ne_2 molecule. Since the nuclei never approach one another closely, the electron groups are virtually those of the separated atoms, retaining their n and l quantum numbers. The configuration might thus be written more explicitly as

$$KK(\sigma_g 2s)^2(\sigma_u 2s)^2(\sigma_g 2p)^2(\pi_u 2p)^4(\pi_g 2p)^4(\sigma_u 2p)^2,$$

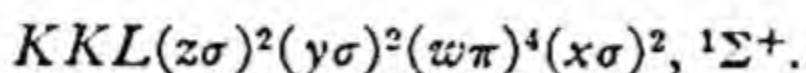
or sometimes simply as $KKLL$, implying completed K and L shells of both atoms with only slight modification of the atomic orbitals. It will be seen later that the $\sigma_u 2p$, $\pi_g 2p$, and other electrons lead to very strong repulsion between atoms; it is for this reason that no stable Ne_2 molecule is known. If it did exist, its ground state would be ${}^1\Sigma_g^+$, since it would consist of closed electronic shells only.

In their ground states, at least, molecules containing atoms in the higher series of the periodic system have electronic configurations which are exactly analogous to those of their lower homologues. For example, the structure of S_2 is similar to that of O_2 ; thus,

$$S_2 [KKLL(z\sigma)^2(y\sigma)^2(x\sigma)^2(w\pi)^4(v\pi)^2, {}^3\Sigma_g^-],$$

where the letters $KKLL$ stand for the twenty electrons, as in the hypothetical Ne_2 molecule, which are virtually unmodified $1s^2$, $2s^2$ and $2p^6$ electrons of the two sulfur atoms making up the S_2 molecule. Apart from these

shells, the electronic arrangement is the same as that for the oxygen molecule, but it must be borne in mind that the letters z , y , x , etc., do not stand for the same quantum numbers as before; they now represent the corresponding series of electrons with a higher value of the principal quantum number. Thus $z\sigma$, $y\sigma$, $x\sigma$, etc., imply modified $\sigma_g 3s$, $\sigma_u 3s$, $\sigma_g 3p$, etc., electrons; in each case the value of n has been changed from 2 to 3. In exactly the same manner, the configurations of P_2 and Cl_2 are analogous to those of N_2 and F_2 , respectively. The structures of the isoelectronic molecules CS , PN and SiO , all of which have $^1\Sigma^+$ ground states, are similar to those of their homologues CO and N_2 ; thus,



One of the atoms, namely C , N or O , of each molecule, is in the first series, while the other, S , P or Si , is in the second series of the periodic classification; the electrons that are virtually unaffected in molecule formation are thus the K and KL groups, respectively, as shown.

Although the ground state of homologous molecules are generally the same, slight differences may occur in the order of the excited states. This is not surprising, for the $w\pi$ and $x\sigma$ electrons are almost equally strongly bound. While in one molecule less energy is required to raise a $w\pi$ electron to a higher level, in the homologue it may be easier to raise one from the $x\sigma$ group. The first excited states will then be different and have different configurations in the two cases. Where definite results are available they can be explained without serious difficulty.

CORRELATION DIAGRAMS

45a. Construction of Correlation Diagrams.—In the foregoing discussion the remarks concerning the stabilities of the various molecular states have been general in nature, but more precise information can be obtained by means of the important *correlation diagrams* developed mainly by Hund⁹ and by Mulliken.¹⁰ In these diagrams the state of an electron in the separated atoms is correlated with that in the united atom, as the nuclei of the former are brought closer together until they coalesce. The construction of these diagrams is based partly on theoretical deductions, and partly on empirical facts derived from a study of molecular spectra.

It was seen in Section 18a that when the electron eigenfunction in the hydrogen molecule-ion is symmetric, a stable state of this ion is possible, but when it is antisymmetric a repulsive state results (Fig. 33). In view of the definition of g and u symmetry character, it is evident that the symmetric electron orbital must have the g property while the antisymmetric orbital has the u character. The $1s$ electron of the hydrogen atom consequently becomes $\sigma_g 1s$ as the two hydrogen nuclei are brought closer to form the stable state ($^2\Sigma_g^+$) of the hydrogen molecule-ion; similarly, in the forma-

⁹ Hund, ref. 4.

¹⁰ Mulliken, ref. 1; see also, Herzberg, ref. 1; Van Vleck and Sherman, ref. 1.

tion of the unstable ($^2\Sigma_u^+$) state the electron orbital becomes $\sigma_u 1s$. As the nuclei come still closer together, the lower energy $\sigma_g 1s$ orbital will, in all probability, pass over into the $1s\sigma$ state; this is the lowest possible orbital, becoming a $1s$ orbital of the united atom. The higher energy $\sigma_u 1s$ electron, however, cannot enter an s orbital in the united atom because of its u

symmetry; it must, therefore, pass into a $2p\sigma$ and finally into a $2p$ orbital. It may consequently be concluded, as shown by Fig. 33, that the $1s\sigma$ orbital is associated with a decrease in potential energy, i.e., attraction, whereas the $2p\sigma$ orbital leads to an increase of potential energy, i.e., repulsion, when formed from a $1s$ orbital in the separated atom.

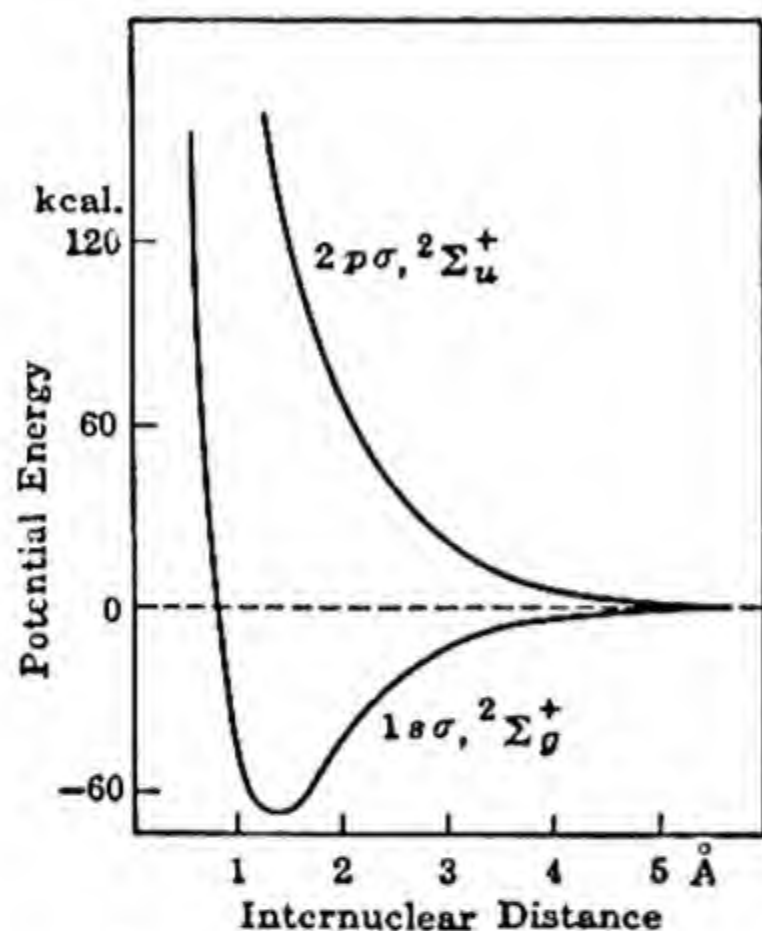


FIG. 33. Potential energy curves for H_2^+

Suppose now that the two hydrogen nuclei are brought so close together that they fuse; the result is an atomic helium ion He^+ . The $1s\sigma$, that is $^2\Sigma_g^+$, state of the hydrogen molecule-ion can give rise only to the 1S_g state of the helium atom-ion, with a $1s$ electron; this would be the stable, low energy, state of the ion. The $2p\sigma$, that is $^2\Sigma_u^+$, state of H_2^+ will, however, be correlated with a 1S_u state of He^+ having a $2p$ electron; this would

represent a much higher energy state. It is possible, therefore, to draw the correlation diagram for the case under consideration, as shown in Fig. 34. In this diagram the ordinates are, qualitatively, potential energies, apart from the effect of nuclear repulsion, and the abscissae give the internuclear dis-

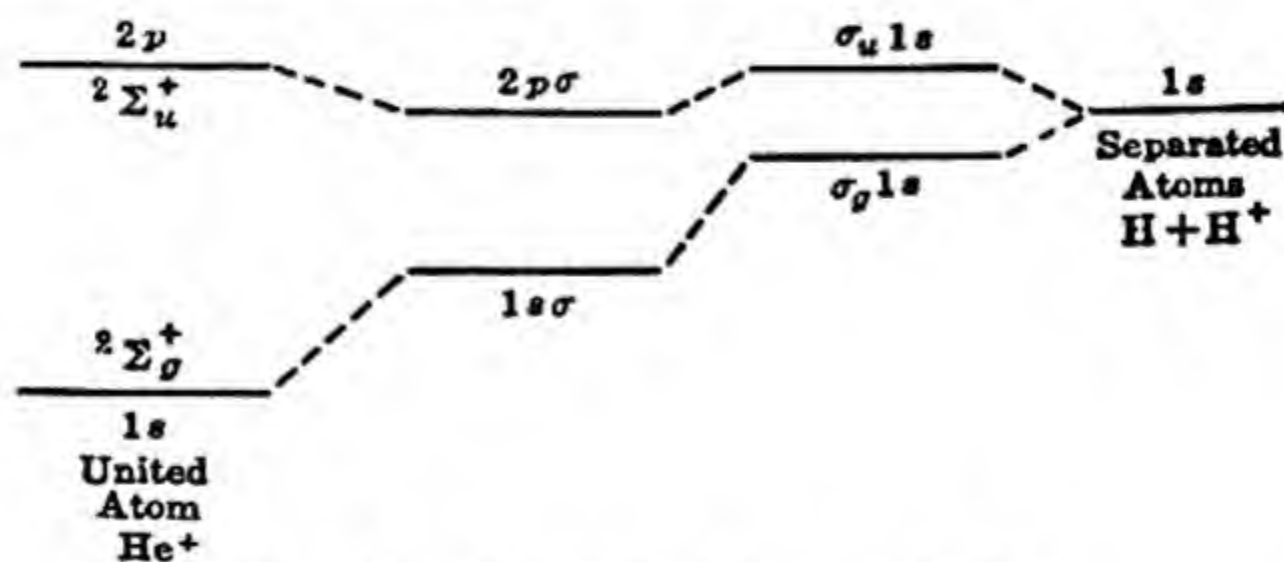


FIG. 34. Correlation diagram for H_2^+

tances. The left-hand side represents the united atom, and the right-hand side corresponds to the separated atoms. Except at these two extremes, the horizontal lines have no real significance, for the transitions are presumably gradual. Between the portions marked $\sigma_g 1s$ (at the right) and $1s\sigma$ (at the left), and between $\sigma_u 1s$ (at the right) and $2p\sigma$ (at the left), the quantum numbers lose their significance, as explained previously.

The steady decrease in potential energy, as the $\sigma_g 1s$ electron of the system with moderately separated hydrogen nuclei passes over into a $1s$ electron of the united atom He^+ , indicates that, in accordance with the wave mechanical calculations (Fig. 33), the $1s\sigma$ electron exerts an appreciable effect in binding together the two nuclei in the hydrogen molecule-ion H_2^+ . On the other hand, the almost horizontal trend of the $\sigma_u 1s$ correlation line implies, again in agreement with calculation, that the $2p\sigma$ electron has a repulsive, rather than a binding, influence. It should be noted that the effect of nuclear repulsion has been excluded from Fig. 34, because this would make all the potential energy curves rise sharply as the nuclei are brought close together. Consequently, a line with a horizontal or slightly downward trend, in going from right to left, actually implies a state of repulsion.

The information derived from Fig. 34 forms the basis of the extended correlation diagrams which attempt to depict the behavior of electrons with higher principal quantum numbers. In the construction of these diagrams it is postulated that the quantum number λ remains unchanged, and for a molecule with identically charged nuclei, the g or u symmetry character of the electron is retained. (It will be recalled that in the united atom, s and d electrons have the u property, whereas p and f electrons have the g symmetry.) It will be seen that these conditions are satisfied in Fig. 34. Further, correlation curves for electrons with different values of λ can cross one another, but curves for the same value of λ , e.g., both σ or both π electrons, cannot cross unless one has g character and the other u character. In other words, the potential energy curves for two σ_g or two σ_u electrons cannot intersect, but a σ_g curve can cross a σ_u curve; a σ_g curve may, however, cross either π_g or π_u , because the λ values are different. The reason for the nonintersection is that at the hypothetical crossing point for identical λ and g (or u), resonance causes the potential curves to spread apart. This is a phenomenon of general occurrence in connection with the question of crossing of potential energy curves of electrons (or electronic systems) in certain analogous states (cf. Fig. 38).

Calculations show that for the same value of n and l , the σ_g level is below σ_u i.e., $\sigma_g 2s$ is below $\sigma_u 2s$, but π_u is below π_g i.e., $\pi_u 2p$ is below $\pi_g 2p$ (cf. Section 40b), at least for relatively large internuclear distances. On the other hand, empirical data, derived from band spectra, show that the $\sigma_g 2p$ orbital is below $\pi_u 2p$; a similar relationship holds for the corresponding $3p$ electrons. It is well known, of course, that the binding energy of atomic electrons decreases in the order $1s, 2s, 2p, 3s$, etc., and this fact is utilized in establishing, more or less empirically, the positions of the extreme right and extreme left of the correlation diagrams. The correlations are made between the lowest possible levels, taking into consideration the limitations expressed in the preceding paragraph. The results obtained for diatomic molecules, along the lines indicated, are shown in Figs. 35 and 36; the former is for equally charged nuclei, and the latter are for unlike nuclei. The difference between the correlation diagrams arises because of the necessity

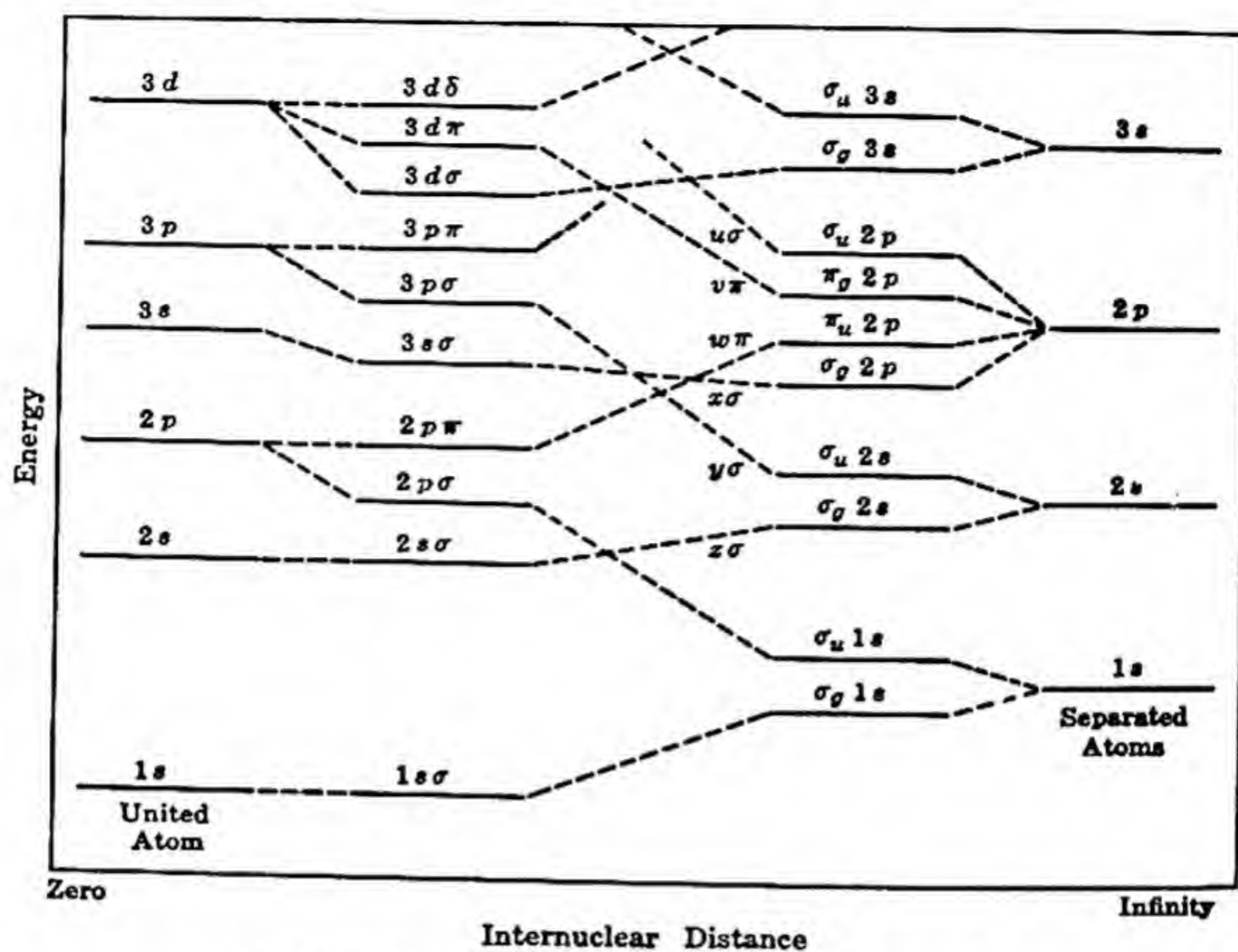


FIG. 35. Correlation diagram: equally charged nuclei

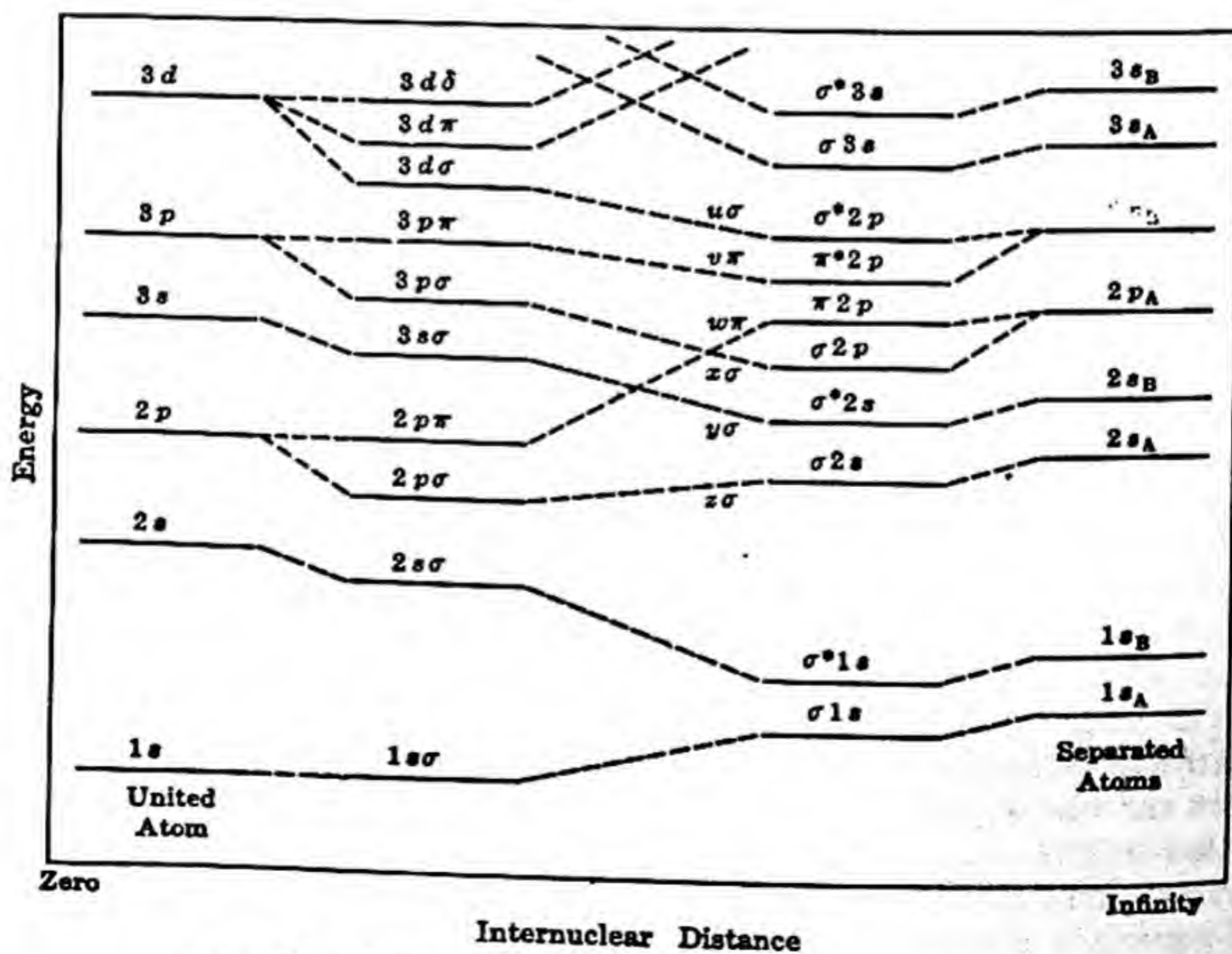


FIG. 36. Correlation diagram: unequally charged nuclei

for taking into account the g and u character of molecules possessing nuclear electrical symmetry. In Fig. 36, for example, it is seen that the correlation of the $1s_B$ orbital in the separated atom with the $2s$ orbital in the united atom is possible when the nuclei are different, but the corresponding correlation, viz., $1s$ to $\sigma_u 1s$ to $2s$ cannot occur, when the nuclei carry equal charges, because the s orbitals in the united atom have g symmetry.

By analogy with the effects of the $\sigma_g 1s$ and $\sigma_u 1s$ electrons in the hydrogen molecule-ion, it is supposed that electron levels, or orbitals, that have a downward trend in passing from the separated atoms to the united atom, that is, from right to left, have a binding effect, whereas those with a horizontal or upward trend have a repulsive influence. Electrons are thus divided roughly into two categories, called *bonding* and *antibonding electrons*, respectively, according as the potential energies decrease or increase (or remain approximately constant) as the nuclei are brought closer together.¹¹ An exact division into the two classes is not possible, for the bonding or antibonding effect is dependent to some extent on the internuclear distance; however, as a general rule the following are bonding electrons:

Equally charged nuclei: $\sigma_g 1s$, $\sigma_g 2s$, ($\sigma_g 2p?$), $\pi_u 2p$, $\sigma_g 3s$, $\pi_u 3p$

Unequally charged nuclei: $\sigma 1s$, $\sigma 2s$, ($\sigma 2p?$), $\pi 2p$, $\pi 3p$.

The corresponding antibonding electrons are:

Equally charged nuclei: $\sigma_u 1s$, $\sigma_u 2s$, $\pi_g 2p$, $\sigma_u 2p$, $\sigma_u 3s$

Unequally charged nuclei: $\sigma^* 1s$, $\sigma^* 2s$, $\pi^* 2p$, $\sigma^* 2p$.

In a stable molecule, the number of bonding electrons may be expected to be larger than the nonbonding type; if the reverse is true, or if the numbers are equal, the molecule will usually be unstable. In certain circumstances, as previously indicated, the innermost electron groups may play no part in holding the nuclei together or in causing them to repel each other; these are the electrons that have been designated by the letters K and L in the electronic configurations. As already mentioned, they are referred to as *nonbonding electrons*, as they have neither bonding nor antibonding effects.

45b. Applications of Correlation Diagrams: Molecular Hydrogen.—

Before proceeding to illustrate the use of the correlation diagrams, it may be noted that although they give a very satisfactory indication of the electronic transitions in molecule formation, they are not always followed exactly. Strictly speaking, the correlations are reliable only when there is one electron outside closed shells, and although they may be used when two or more such electrons are involved, there are instances known of the occurrence of correlations that are apparently not permitted by the diagrams. Reference will be made shortly to one or two cases of this kind. However, even in these instances the g and u , and $+$ and $-$, symmetry properties of the electronic state as a whole are preserved, as also are the Λ and S values, so that the term type is in accordance with prediction. The correlations are therefore applicable to the whole state rather than to the individual electrons.

¹¹ Herzberg, ref. 4; Hund, *Z. Physik*, 63, 719 (1930).

It was seen in Section 42a that the normal $(1s\sigma)^2, {}^1\Sigma_g^+$ state of molecular hydrogen is derived from two $\sigma_g 1s$ (or $1s\sigma$) electrons; since both of these have a bonding effect, the stability of the resulting molecule is readily understood. On the other hand, the unstable $(1s\sigma)(2p\sigma), {}^3\Sigma_u^+$ state is derived from one $\sigma_g 1s$ (or $1s\sigma$) and one $\sigma_u 1s$ (or $2p\sigma$) electron; the former is bonding but the latter is antibonding, and so the resulting form of molecular hydrogen would not be expected to have any appreciable stability. The qualitative results

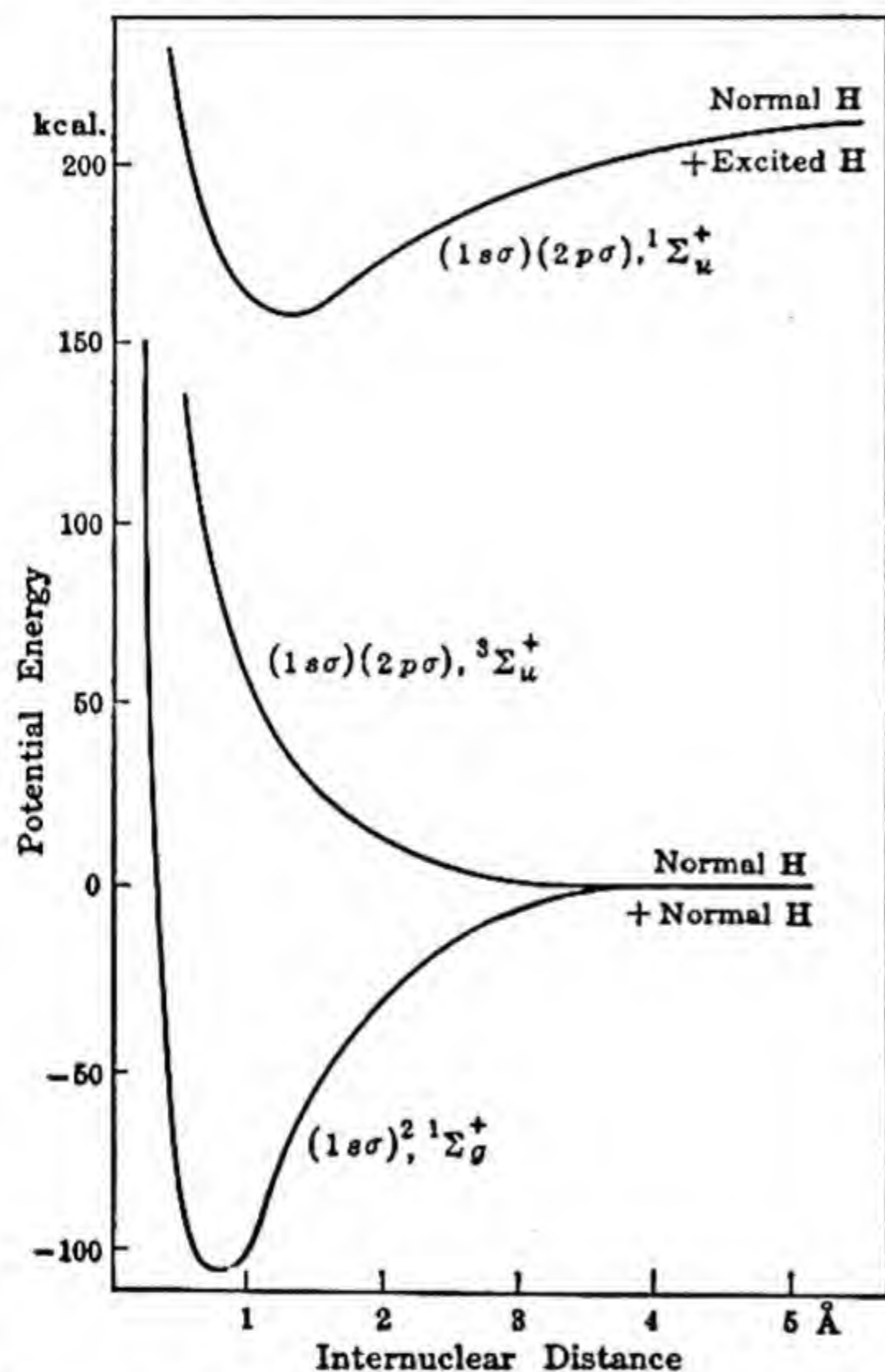


FIG. 37. Potential energy curves of the H_2 molecule

atoms, this orbital is now no longer antibonding. The result is that the ${}^1\Sigma_u^+$ state of molecular hydrogen is stable relative to one normal and one excited, either 2S or 2P , hydrogen atom (Fig. 37), although the ${}^3\Sigma_u^+$ state with the same electronic configuration is unstable with respect to two normal atoms. It is a relatively common occurrence for a particular molecular electronic configuration to represent a system that is unstable with respect to two normal atoms, while the same configuration may be stable relative to one or more excited atoms. It has been indicated earlier that the state with the highest multiplicity, for a given electronic configuration, is the one with the lowest

derived in this manner are seen to be identical with those reached by the method of Heitler and London, as described in Chapter III.

It has been noted previously that another state, viz., ${}^1\Sigma_u^+$, arises from the configuration $(1s\sigma)(2p\sigma)$; this state, however, does not dissociate into two normal hydrogen atoms, but into one normal and one excited atom, with either a $2s$ or a $2p$ electron. Actually, according to the correlation diagram in Fig. 35, neither of the configurations $1s2s$ or $1s2p$ can give rise to $(1s\sigma)(2p\sigma)$. It is probable that the $2s$ (or $2p$) electron becomes $3p\sigma$ (or $3s\sigma$), but as the lower energy orbital $2p\sigma$ is available, the electron passes to this level, which it can do without either changing the symmetry character or the Λ and S values of the molecule. Since the $2p\sigma$ level is not above, and may even be below, the $2s$ or $2p$ level of the separated

potential energy in its equilibrium state; that this is true in the case under consideration is shown by the potential energy diagram in Fig. 37.

45c. The Diatomic Helium Molecule.—When two normal ($1s^2, ^1S$) helium atoms are brought together there are available four $1s$ electrons; two of these will probably enter the lowest available, i.e., $\sigma_g 1s$ level, and the other two will occupy the next, i.e., $\sigma_u 1s$ level. Since two $\sigma_g 1s$ electrons have a bonding effect while two $\sigma_u 1s$ electrons are antibonding, the helium molecule He_2 should be unstable relative to two normal helium atoms, as is indeed the case. According to the correlation diagram (Fig. 35) the two $\sigma_g 1s$ electrons should go over into $(1s\sigma)^2$ and the two $\sigma_u 1s$ electrons into $(2p\sigma)^2$, so that the configuration should be $(1s\sigma)^2(2p\sigma)^2$. In this case, however, another factor is introduced by the possible crossing of two curves. If two excited ($1s2s, ^3S$) helium atoms are brought together, there are avail-

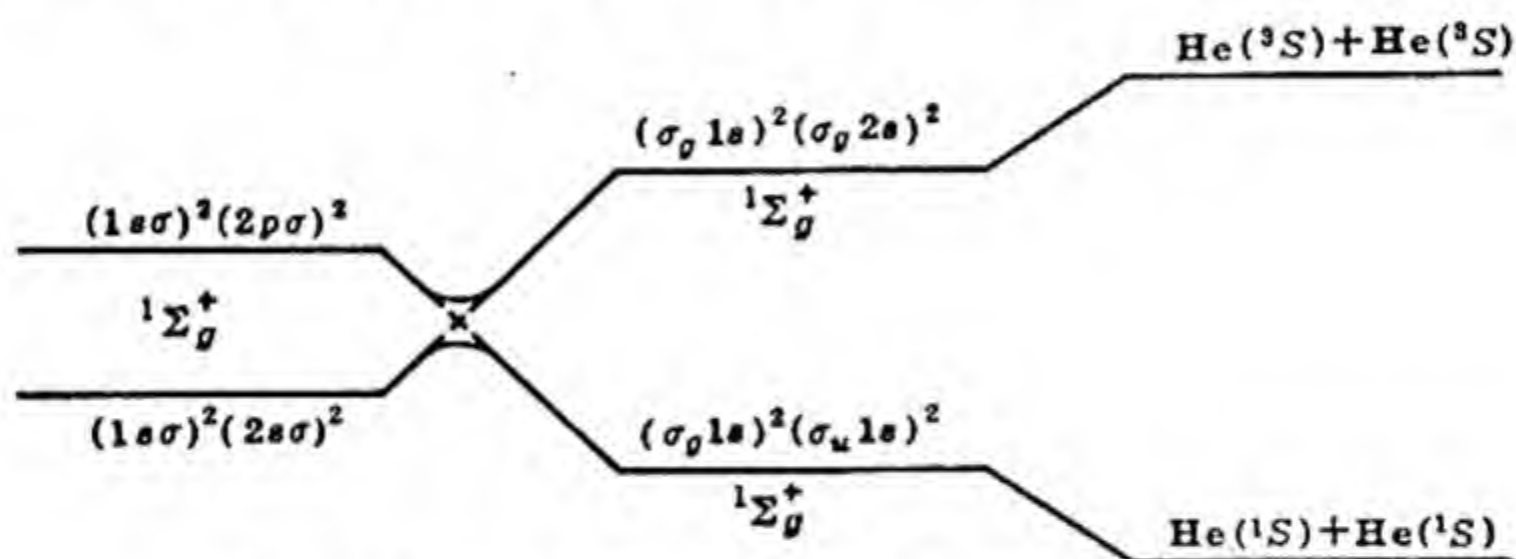


FIG. 38. Correlation diagram for the He_2 molecule

able two $\sigma_g 1s$ and two $\sigma_g 2s$ orbitals; these should pass over into the configuration $(1s\sigma)^2(2s\sigma)^2$, which lies below the level of the configuration $(1s\sigma)^2(2p\sigma)^2$ derived from two normal helium atoms. If there were no interaction the two correlation curves should cross, but as both systems represent $^1\Sigma_g^+$ states, resonance occurs and consequently the curves tend to avoid each other, as shown in Fig. 38. The result is that the combination of the two normal (1S) helium atoms gives rise to the $(1s\sigma)^2(2s\sigma)^2, ^1\Sigma_g^+$ state of the molecule He_2 . On the other hand, the two excited atoms yield the molecule with the configuration $(1s\sigma)^2(2p\sigma)^2, ^1\Sigma_g^+$.

It should be noted that the $(1s\sigma)^2(2s\sigma)^2$ state will be unstable with respect to normal helium atoms in spite of the fact that the $2s\sigma$ orbitals are often bonding; the reason for this is that the electrons occupying these orbitals were in the $1s$ state of the atom, and hence had a much lower potential energy than they have in the molecule. The $(1s\sigma)^2(2p\sigma)^2$ form of the He_2 molecule will undoubtedly be unstable with respect to normal helium atoms, but it may be stable relative to two excited atoms.

Combination of a normal ($1s^2, ^1S$) helium atom and an excited ($1s2s, ^3S$) atom gives at large internuclear distances $(\sigma_g 1s)^2(\sigma_u 1s)(\sigma_g 2s)$, which becomes $(1s\sigma)^2(2p\sigma)(2s\sigma)$. In this configuration there are three bonding electrons, $(1s\sigma)^2$ and $2s\sigma$, the latter arising from a $2s$ orbital, and one antibonding electron, $2p\sigma$. The molecule He_2 , which will be in a $^3\Sigma_u^+$ state, should thus

be stable with respect to a normal and an excited atom. Spectroscopic studies show that a state of this type actually exists.

In the helium molecule-ion He_2^+ there are only three electrons, and these must be $(\sigma_g 1s)^2(\sigma_u 1s)$, which become $(1s\sigma)^2(2p\sigma)$ according to the correlation diagram; this configuration will represent a ${}^2\Sigma_u^+$ state. In this ion there are two bonding $1s\sigma$ electrons and one nonbonding $2p\sigma$ electron; it is to be expected that He_2^+ will be stable with respect to a normal helium atom and a helium ion. Spectroscopic data confirm this expectation. It is remarkable that the absence of one antibonding electron, as compared with the normal He_2 molecule, makes the He_2^+ ion stable. Attention should be called to the fact that the transition of the $\sigma_u 1s$ orbital to $2s\sigma$ that occurs in the He_2 molecule, as shown in Fig. 38, cannot take place in the ion He_2^+ because the electron would thereby change its u character. In this case, therefore, the crossing of the type prohibited in Fig. 38 is permitted.

45d. Molecules of the First Period.—Examination of the structure of the normal nitrogen molecule (Section 43b) shows that it has four nonbonding (KK) electrons which are virtually unchanged atomic electrons, having no appreciable influence on the structure of the molecule. Of the others, the eight electrons $(z\sigma)^2$, $(x\sigma)^2$ and $(w\pi)^4$ are bonding, while the $(y\sigma)^2$ electrons are nonbonding; the net result is thus equivalent to six bonding electrons. The nitrogen molecule in its ground state is, therefore, very stable with respect to two normal nitrogen atoms. The same considerations apply to carbon monoxide.

In their lowest and second lowest states, the isoelectronic systems, BO , CO^+ , CN and N_2^+ have seven bonding and two antibonding electrons; hence these molecules are relatively stable with respect to the normal atoms, or ions, into which they dissociate. The third lowest (second excited) state has apparently eight bonding electrons, $(z\sigma)^2$, $(w\pi)^4$ and $(x\sigma)^2$, and one antibonding electron, $y\sigma$; considerable stability is, therefore, to be expected, and is actually found. It might be imagined, at first sight, that since the net number of bonding electrons is seven, compared with five in the other states, that the energy required for the dissociation would be greater in the former than in the latter. The difference between the heats of dissociation is not large, but the values are certainly not in the expected order. One reason for this, which must always be borne in mind, is that the bonding and antibonding powers of electrons vary with the distance between the nuclei. The $x\sigma$ electrons, for example, are never very strongly bonding, and may actually have some antibonding effect at small internuclear distances; at the same time the repulsive influence of $y\sigma$ electrons may increase. It is thus possible for the second excited states of the molecules BO , CO^+ , CN and N_2^+ to have smaller dissociation energies than the lower states, despite the fact that the former apparently possess a larger net number of bonding electrons.

In passing from molecular nitrogen to molecular oxygen, two $v\pi$ electrons are added; these are antibonding at nearly all internuclear distances, and so the oxygen molecule has eight bonding electrons and four anti-

bonding electrons. The excess of the former accounts for the great stability of the oxygen molecule in its normal ($^3\Sigma_g^-$) state. In the excited ($^3\Sigma_u^-$) state, the bonding electrons are decreased by one ($w\pi$), while the antibonding electrons ($v\pi$) are increased by the same number. The energy of dissociation in this state is therefore much less than in the normal state, in spite of some compensation due to the fact that an excited atom results in the former case.

It has been seen in Section 44c that the formation of the ground state of the ion O_2^+ may be regarded as being due to the loss of a $v\pi$ electron from the normal oxygen molecule. In this event, the O_2^+ ion should possess eight bonding electrons, as does the molecule, but one fewer, namely three, antibonding electrons, leaving an excess of five bonding electrons in the ion. The energy required to dissociate the oxygen molecule-ion into an oxygen atom and an atomic oxygen ion, in their ground states, should be greater than that required to break up the oxygen molecule into two normal atoms. This has been found to be the case, as will be seen shortly.

It is perhaps unnecessary to remark that the correlation scheme does not apply to hydrides; the electronic structures of these substances have been already considered in Section 42.

45e. Bonding Electrons and Valence.—It has been suggested by Herzberg (1929) that the ordinary chemical valence of a bond is equal to the number of pairs of bonding electrons in excess of the number of pairs of antibonding electrons. Further, the difference in these two numbers may be regarded as an approximate measure of the bond energy. These suggestions may be tested by means of the data in Table XVII, which refer to

TABLE XVII. VALENCE AND BONDING AND ANTIBONDING ELECTRON PAIRS

Molecule	Bonding Pairs	Antibonding Pairs	Difference	Chemical Valence	Heat of Dissociation
CO	4	1	3	3	9.14 e.v.
N ₂	4	1	3	3	7.38
N ₂ ⁺	3½	1	2½	—	6.35
NO	4	1½	2½	—	5.29
O ₂ ⁺	4	1½	2½	—	6.48
O ₂	4	2	2	2	5.08
H ₂	1	0	1	1	4.48
H ₂ ⁺	½	0	½	—	2.65

the lowest energy states of a number of diatomic molecules and ions. The results for the hydrogen molecule and the hydrogen molecule-ion, although these substances contain no antibonding electrons, are also included in the table for purposes of comparison.

It is seen that the difference between the bonding and antibonding pairs is equal to the number of ordinary valence bonds in the molecules concerned, where the valence is known. The bonding between carbon and oxygen in carbon monoxide is equivalent to a triple bond, in agreement with the modern chemical formulation as involving resonance between double bonded and triple bonded configurations. In nitric oxide the nitrogen and oxygen atoms are held together by the equivalent of two and one-half valence

bonds; this is in harmony with the suggestion that in this compound there are two normal (two-electron) bonds and one three-electron bond with the bonding power of a single-electron bond.¹²

For molecules involving similar electron groups, such as N_2 , O_2 , N_2^+ and O_2^+ , the heat of dissociation is approximately proportional to the difference between the numbers of bonding and antibonding pairs. The proportionality is not so good when O_2 is compared with H_2 , but it must be remembered that electrons with different principal quantum numbers are involved. When comparing H_2 with H_2^+ , however, the rough proportionality between heat of dissociation and the excess of bonding pairs is again apparent. It is obvious, of course, that the generalization concerning bond strengths is meant to serve only as an approximate guide, for the bonding effects of different pairs of electrons are not necessarily equal, and neither will their influence be compensated exactly by the effect of the antibonding pairs.

¹² Pauling, *J. Am. Chem. Soc.*, 53, 3225 (1931).

CHAPTER VII

STATISTICAL MECHANICS ¹

GENERALIZED COORDINATES IN PHASE SPACE

46a. Introduction.—The function of statistical mechanics in the field of physical science is analogous to that of statistics as applied to biological phenomena. Although the behavior of any one individual cannot be foretold, it is nevertheless possible to predict the average properties, in the statistical sense, of a considerable number of such individuals. If the positions and velocities of all the molecules in a given volume of gas were known, it should be possible, in principle, to determine their future behavior by applying the familiar laws of mechanics. Nevertheless, because of the large number of such molecules present in the volume of gas, the calculations would prove to be insuperably difficult. Of course, in actual practice the position and velocity of each of the gas molecules cannot be known, yet by applying the methods of statistical mechanics, the average, or most probable, behavior of a given system containing a large number of these molecules can be predicted. Essentially the methods of statistical mechanics involve the application of the fundamental laws of mechanics to systems which are so complex that the practical application of those laws in detail to the component parts of the system would be quite out of the question. Statistical mechanics thus makes it possible to obtain information concerning the properties of a system without the necessity of a too intimate knowledge of the characteristics of the component parts of the system.

In the realm of physical observation it is customary to take a number of measurements of an observable quantity, and then to derive from these the weighted average or most probable value of the given quantity. The same principle is applied in statistical mechanics. Instead of attempting to consider the behavior of a single system, it is the practice to study a collection of a large number of such systems, generally referred to as an *ensemble of systems*. All the members of the ensemble will have the same "structure"; in other words, they must be identical with respect to such properties as the size and shape of the containing vessel, the number of molecules, total energy, etc. However, the systems will be distributed over a range of states, i.e., they *differ in phase*; that is to say, the coordinates and velocities of the molecules differ from one system to another. Although the behavior of any one sample cannot be predicted, it is nevertheless possible to draw conclusions concerning the statistical behavior of the whole ensemble, and

¹ Fowler, "Statistical Mechanics"; Fowler and Guggenheim, "Statistical Thermodynamics"; Kennard, "Kinetic Theory of Gases"; Mayer and Mayer, "Statistical Mechanics"; Tolman, "The Principles of Statistical Mechanics."

hence as to the *probable* behavior of the single system of interest. It should be emphasized that statistical mechanics cannot provide information regarding the *actual* behavior of this system; it merely indicates what situation has the greatest probability. However, if the number of systems in the ensemble is very large, the difference between the most probable behavior and that actually observed will be quite negligible. Of course, a certain number of systems will have properties that differ from the statistical average, but this number is very low, and the probability of their being encountered is extremely small.

In the treatment which follows it will be assumed, in the first place, that the laws of classical mechanics apply to the movement of the molecules. Later, such modifications as are made necessary by quantum mechanics will be considered, and it will be shown that under conditions of general interest to chemists the changes are negligible. The introduction of the quantum theory of energy, however, leading to the development of quantum statistical mechanics, has had important consequences; one of the greatest triumphs has been the calculation of thermodynamic quantities of elements and molecules from spectroscopic data.

46b. Phase Space.—According to classical mechanics the state of a system at any time may be completely defined by specifying the positions and velocities of all its component parts. The position of a single atom can be defined by three cartesian coordinates x, y, z , and the magnitude and direction of its velocity can be stated in terms of the velocity components $\dot{x}, \dot{y}, \dot{z}$. In general, if f coordinates are required to indicate the position at any instant of all parts of a system, consisting perhaps of a very large number of molecules, it will be necessary to specify, in addition, f velocity components, in order that the system may be defined completely. The system is then said to possess f *degrees of freedom*. It will be apparent, of course, that in considering the position of a point in space, the definition is not restricted to the use of three cartesian coordinates; any appropriate coordinates may be chosen according to circumstances, but it is always true that three independent coordinates, using the term in a general sense, are necessary. Similarly, when the system has f degrees of freedom, the position can be defined by means of f *generalized coordinates*, which may be represented by

$$q_1, q_2, q_3, \dots, q_f.$$

Corresponding to these coordinates there are f generalized velocities $\dot{q}_1, \dot{q}_2, \dot{q}_3, \dots, \dot{q}_f$, but for reasons which will be made clear shortly, it is the practice in statistical mechanics to employ momenta in place of velocities; thus, the f generalized momenta, necessary to specify the motions of all the component parts of the system under consideration, are

$$p_1, p_2, p_3, \dots, p_f.$$

In order to facilitate the application of the laws of mechanics to all parts of a system simultaneously, it is convenient to invent a scheme which can

be used to represent the state (or *phase*) of each system in an ensemble, as well as the condition of the whole ensemble. This can be done by imagining a conceptual euclidean space having $2f$ dimensions; this space, known as *phase space* or γ -space, is supposed to have $2f$ rectangular axes, one for each of the f generalized coordinates, q_1, q_2, \dots, q_f , and one for each of the corresponding momenta, p_1, p_2, \dots, p_f . It is thus possible to define completely the instantaneous state of any system of f degrees of freedom by means of a representative point, called a *phase point*, in this $2f$ -dimensional hyperspace. The changes in phase, i.e., of the coordinates and momenta, of the system can then be represented by a trajectory in phase space. In this space the ensemble of systems appears as a "dust cloud," consisting of a large number of points, and its behavior in the course of time is associated with the streaming motion of the cloud.

46c. Density of Distribution in Phase Space.—In an ensemble of systems there is no need to distinguish between the individual systems, for in statistical mechanics the essential interest lies in the numbers of systems to be found in different states, that is, in different regions of the γ -space, at any given time. Hence, the condition of an ensemble can be suitably described in terms of the *density* with which the representative (phase) points are distributed in the γ -space. It should be noted that by supposing the ensemble to contain a very large number of members, there is a virtually continuous, rather than a discontinuous, change in the number of systems in passing from one region of γ -space to another. The density of the points in the γ -space can thus be treated as a continuous function.

In an ensemble possessing f degrees of freedom, the density of distribution ρ of the phase points is a function of the $2f$ coordinates and momenta, viz., $q_1, q_2, \dots, q_f, p_1, p_2, \dots, p_f$, corresponding to the $2f$ axes in the γ -space. It is also a function of the time t , since the movement of the phase points, corresponding to changes in coordinates and momenta, will result in changes of the distribution density at any given point. It is possible to write, therefore,

$$\rho = \rho(q_1, \dots, q_f, p_1, \dots, p_f, t), \quad (46.1)$$

or, in brief,

$$\rho = \rho(q, p, t). \quad (46.2)$$

The significance of the quantity ρ is that it is a measure of the number of systems that are to be found at a given point represented by $q_1, \dots, q_f, p_1, \dots, p_f$, or more exactly, in a given infinitesimally small region of the γ -space. This region is one in which the coordinates lie between q_1 and $q_1 + \delta q_1$, q_2 and $q_2 + \delta q_2$, \dots , q_f and $q_f + \delta q_f$, and the momenta between p_1 and $p_1 + \delta p_1$, p_2 and $p_2 + \delta p_2$, \dots , p_f and $p_f + \delta p_f$, and its hypervolume will be $\delta q_1 \delta q_2 \dots \delta q_f \delta p_1 \delta p_2 \dots \delta p_f$; the product of this volume by the density ρ gives the number of systems δN lying in the specified region, viz.,

$$\delta N = \rho \delta q_1 \dots \delta q_f \delta p_1 \dots \delta p_f. \quad (46.3)$$

As noted above, the total number of systems in the ensemble is so large that

ρ and δN can be considered to change continuously in passing from one region of γ -space to another.

46d. Liouville's Theorem.—It is of primary importance in the further development of statistical mechanics to know how the density ρ changes with time, and for this purpose use is made of a mathematical theorem first propounded by Liouville (1838) in another connection. It may be noted, incidentally, that it is in relation to the derivation of the rate of change of density with time, that the principles of classical mechanics are introduced into the statistical treatment of an ensemble of systems.

Consider the small element of hypervolume $\delta q_1 \cdots \delta q_f \delta p_1 \cdots \delta p_f$ situated at the point whose coordinates are $q_1, \dots, q_f, p_1, \dots, p_f$ in the γ -space; the number δN of phase points in this element is given by equation (46.3). As a result of movements of these points in the γ -space, there will be, in general, a change in this number with time. This change will occur if the number of phase points entering the volume through any "face" is different from the number leaving the opposite "face." Consider two faces normal to the q_1 axis with coordinates q_1 and $q_1 + \delta q_1$; the number of phase points entering the former face in unit time will be

$$\rho \dot{q}_1 \delta q_2 \cdots \delta q_f \delta p_1 \cdots \delta p_f,$$

where \dot{q}_1 is the component of velocity, in the direction of the q_1 axis, of representative points at $q_1, \dots, q_f, p_1, \dots, p_f$. In exactly the same manner, the number of phase points leaving the opposite face is seen to be

$$\left(\rho + \frac{\partial \rho}{\partial q_1} \delta q_1 \right) \left(\dot{q}_1 + \frac{\partial \dot{q}_1}{\partial q_1} \delta q_1 \right) \delta q_2 \cdots \delta q_f \delta p_1 \cdots \delta p_f.$$

Subtraction of the latter expression from the former gives the rate of change in the number of phase points δN in the element of hypervolume, i.e., $d(\delta N)/dt$, as far as the q_1 coordinate is concerned; neglecting second order differentials, this difference is

$$- \rho \left(\frac{\partial \dot{q}_1}{\partial q_1} + \frac{\partial \rho}{\partial q_1} \dot{q}_1 \right) \delta q_1 \cdots \delta q_f \delta p_1 \cdots \delta p_f.$$

For the p_1 coordinate, there will be a similar expression

$$- \rho \left(\frac{\partial \dot{p}_1}{\partial p_1} + \frac{\partial \rho}{\partial p_1} \dot{p}_1 \right) \delta q_1 \cdots \delta q_f \delta p_1 \cdots \delta p_f,$$

and summing all the terms for the f coordinates and the f momenta, it follows that the total rate of change in the number of representative points in the given element of γ -space is

$$\begin{aligned} \frac{d(\delta N)}{dt} = & - \sum_{i=1}^f \left\{ \rho \left(\frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i} \right) \right. \\ & \left. + \left(\frac{\partial \rho}{\partial q_i} \dot{q}_i + \frac{\partial \rho}{\partial p_i} \dot{p}_i \right) \right\} \delta q_1 \cdots \delta q_f \delta p_1 \cdots \delta p_f. \quad (46.4) \end{aligned}$$

The Hamiltonian (or canonical) equations of motion, derived from classical mechanics, are

$$\dot{q}_i = \frac{\partial H}{\partial p_i} \quad \text{and} \quad \dot{p}_i = -\frac{\partial H}{\partial q_i}, \quad (46.5)$$

where H represents the Hamiltonian function, i.e., the total energy expressed as a function of the p 's and q 's. These equations may be applied to the motion of the representative point in the $2f$ -dimensional hyperspace, and as a result a considerable simplification of equation (46.4) is possible. Since the order of differentiation is immaterial, it follows, from the equations (46.5), by taking the derivative of \dot{q}_i with respect to q_i , and of \dot{p}_i with respect to p_i , that

$$\frac{\partial \dot{q}_i}{\partial q_i} = -\frac{\partial \dot{p}_i}{\partial p_i} = \frac{\partial^2 H}{\partial q_i \partial p_i}$$

or

$$\sum_i \left(\frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i} \right) = 0.$$

Introduction of this result into equation (46.4) then leads to the cancellation of the term in the first set of parentheses on the right-hand side. If the resultant expression is now divided through by the volume $\delta q_1 \cdots \delta q_f \delta p_1 \cdots \delta p_f$, there will be obtained, according to equation (46.3), the rate of change of density, i.e., $\partial \rho / \partial t$, at the point under consideration; thus

$$\left(\frac{\partial \rho}{\partial t} \right)_{q,p} = - \sum_i \left(\frac{\partial \rho}{\partial q_i} \dot{q}_i + \frac{\partial \rho}{\partial p_i} \dot{p}_i \right). \quad (46.6)$$

As already seen, the density ρ is a function of q , p and t ; since the point at which the rate of change of density is being observed is a fixed one, it follows that all the coordinates in the γ -space are fixed. The use of the partial differential notation on the left-hand side of equation (46.6) is consequently justified.

The relationship, equation (46.6), giving the rate of change of density at a fixed point in the γ -space is generally known as Liouville's theorem, as applied to the problems of statistical mechanics. By a slight rearrangement, equation (46.6) becomes

$$\left(\frac{\partial \rho}{\partial t} \right)_{q,p} + \sum_i \frac{\partial \rho}{\partial q_i} \dot{q}_i + \sum_i \frac{\partial \rho}{\partial p_i} \dot{p}_i = 0, \quad (46.7)$$

in which the first term, as just seen, gives the rate of change of the density, when all the p 's and q 's are fixed. Remembering that \dot{q}_i is really $\partial q_i / \partial t$, and that \dot{p}_i is $\partial p_i / \partial t$, it is apparent that the second and third terms in equation (46.7) give $\partial \rho / \partial t$, for constant p , and for constant q , respectively, i.e.,

$$\sum_i \frac{\partial \rho}{\partial q_i} \dot{q}_i = \left(\frac{\partial \rho}{\partial t} \right)_{p,t} \quad \text{and} \quad \sum_i \frac{\partial \rho}{\partial p_i} \dot{p}_i = \left(\frac{\partial \rho}{\partial t} \right)_{q,t}.$$

The sum of the three terms on the left-hand side of equation (46.7) is thus equal to the *total* rate of change of density in the vicinity of a moving point; according to the equation this sum must be zero, and hence it is possible to write

$$\frac{d\rho}{dt} = 0. \quad (46.8)$$

The rate of change of density in the immediate vicinity of any given phase point as it moves through γ -space is thus zero. This important conclusion, reached from Liouville's theorem, has been called the *principle of the conservation of density in phase*.

The result of equation (46.8) can be used to derive another fundamental principle of statistical mechanics. Consider a region in γ -space which, although finite, is small enough for the density ρ to be treated as uniform throughout; if the hypervolume of the region is δv , the number δN of representative (phase) points in this region will be given by

$$\delta N = \rho \delta v. \quad (46.9)$$

On differentiating this expression with respect to t , it is seen that

$$\frac{d(\delta N)}{dt} = \frac{d\rho}{dt} \delta v + \rho \frac{d(\delta v)}{dt}. \quad (46.10)$$

If it is supposed that the boundaries of the region under consideration are permanently determined by the phase points that were originally on the surface, then no points can enter or leave this region. In other words, the points on the outer surface act as a sort of continuous thin skin by which all the points in the region are enclosed. Further, since each phase point represents a definite system, these points can neither be created nor destroyed. It follows, therefore, that the number δN of points in the region studied must always remain constant; consequently, $d(\delta N)/dt$ is zero, and equation (46.10) becomes

$$\frac{d\rho}{dt} \delta v + \rho \frac{d(\delta v)}{dt} = 0. \quad (46.11)$$

According to equation (46.8), $d\rho/dt$ is zero, and hence

$$\frac{d(\delta v)}{dt} = 0, \quad (46.12)$$

which means that the volume in γ -space of the particular region, occupied by a definite number of phase points, does not change with time. The shape of the region may change considerably and without restriction, corresponding to changes in phase of the constituent systems, but the volume enclosed by the hypothetical "skin" remains unaltered. Although this result was proved, strictly, for a small region of uniform density, it is possible to extend

it to any region, for the latter may be regarded as made up of a number of small regions. The conclusion expressed in equation (46.12), of the constancy of the volume of any extension in γ -space, has been called the *principle of the conservation of extension in phase*.

It may be pointed out here that the simple fundamental principles, concerning the constancy of density and of extension in phase, depend entirely on the choice of generalized coordinates and momenta as the axes for the phase (γ) space. If velocities had been chosen instead of momenta, the conclusions reached would have been much more complex. This is the reason, referred to previously, for the choice of coordinates and momenta as the means of representing the state of a system.

46e. Statistical Equilibrium.—An ensemble is said to be in *statistical equilibrium* when the probabilities of finding the phase points in the various regions of the γ -space are independent of time. Under these conditions the average values of the properties of the system in the ensemble also do not change with time. Ensembles in statistical equilibrium are thus of particular significance to chemistry.

Expressed in mathematical terms, for an ensemble in statistical equilibrium, the density ρ would be independent of time at all points in the γ -space; that is,

$$\left(\frac{\partial \rho}{\partial t} \right)_{q, p} = 0 \quad (46.13)$$

for all values of q and p . The problem of interest is to find what function ρ must be in order to satisfy the condition represented by equation (46.13). Actually several different functions, corresponding to different types of ensemble, are possible. In the type which will be employed in the present treatment, the density ρ will be taken as a function of some property of the motion of the systems, e.g., the energy; representing this property by α , the density can be expressed as

$$\rho = \rho(\alpha),$$

and hence the Liouville theorem, equation (46.6), takes the form

$$\left(\frac{\partial \rho}{\partial t} \right)_{q, p} = - \frac{d\rho}{d\alpha} \sum_i \left(\frac{\partial \alpha}{\partial q_i} \dot{q}_i + \frac{\partial \alpha}{\partial p_i} \dot{p}_i \right). \quad (46.14)$$

The property α is one which is a function of the coordinates and momenta, but the value for any given system would not change with time, i.e., $d\alpha/dt$ is zero; hence, from equation (46.14), it is possible to write

$$\frac{d\alpha}{dt} = \sum_i \left(\frac{\partial \alpha}{\partial q_i} \dot{q}_i + \frac{\partial \alpha}{\partial p_i} \dot{p}_i \right) = 0, \quad (46.15)$$

where \dot{q}_i and \dot{p}_i are to be regarded as the rates of change with time of the coordinates q_i and p_i of a phase point as a result of the natural motion which

such points may undergo. It is thus possible to combine equations (46.14) and (46.15), with the result

$$\left(\frac{\partial \rho}{\partial t}\right)_{q, p} = 0,$$

and since the position of the fixed point, represented by q and p , has not been specified, this relationship will hold for any point in the γ -space. This is just the condition for statistical equilibrium expressed by equation (46.13), and hence it is evident that if the density ρ is a function of some property of the motion of the systems that is independent of time, the ensemble of systems will be in statistical equilibrium.

46f. The Microcanonical Ensemble.—A particular type of ensemble that is especially useful for present purposes, and satisfies the necessary conditions for statistical equilibrium, is that known as the *microcanonical ensemble*. For the so-called *conservative systems*, which are those most frequently encountered, the energy is a property of the motion; hence, for such systems an ensemble, with the density ρ distributed as any function of the energy E , would be in statistical equilibrium. In the microcanonical ensemble, the density is taken as equal to zero for all values of the energy except those lying in a particular narrow range from E to $E + \delta E$; that is to say, for the microcanonical ensemble

$$\begin{aligned}\rho &= \text{constant, in the range } E \text{ to } E + \delta E \\ \rho &= \text{zero, outside this range.}\end{aligned}$$

Since the density is a function of the energy in ensembles of this type, it is apparent that they will be in statistical equilibrium. The most probable or average values of the properties which are predicted for any system belonging to a microcanonical ensemble will thus not vary with time. A microcanonical ensemble can consequently be considered as representing a system which is apparently in a steady condition, at least when examined macroscopically so that the behavior of the individual molecules is not observed.

It may be remarked that the points of constant energy lie on a definite surface in γ -space. It follows, therefore, that the phase points representing a microcanonical ensemble must all occur in the narrow shell lying between the two surfaces corresponding to the constant energies E and $E + \delta E$. In this shell the density is constant, and hence the distribution of phase points is uniform; according to Liouville's theorem, it remains so at all times.

47a. Postulate of Equal Probabilities.—So far in the development of the statistical mechanics, the methods used have been based essentially on the principles of classical mechanics. In order to go further, however, in the application to molecular systems, it is necessary to introduce a postulate of some kind. Such a postulate will be incapable of direct proof, but it must be one that, at least, appears to be reasonable in character. The ultimate justification of the postulate will be found in the agreement between experi-

mental observations and the predictions made with its aid. It must be realized that the necessity for this postulate is not to be ascribed to any inadequacy in the principles of mechanics that have been employed; it must be attributed, rather, to the incompleteness of the knowledge concerning the systems under consideration. In all applications of statistical mechanics, whether they be associated with mechanical or other problems, there must be available some information relative to the "weighting" of different states or individual occurrences. It is in connection with this weighting, or *a priori probability*, that the postulate, to be described below, will be made.

In the early discussions of statistical mechanics there was proposed what became known as the *ergodic hypothesis* of Boltzmann, or the postulate of the *continuity of path* of Maxwell. According to these assumptions, it was supposed that the phase point of any isolated system would pass in turn through every point compatible with the energy of the system, before returning to its original position in γ -space. The essential consequence of this postulate is that the probability of any given system being in a specified state, at a random instant of time, would be identical with the probability of a system, chosen at random from the appropriate ensemble, being in that same state. In other words, the average property of a system at any instant of time would be the same as the ensemble average. Since the property observed experimentally is really a time average, it follows, according to the ergodic hypothesis, that the ensemble average for a given property, as derived from statistical mechanics, should correspond to the observed value.

There are many reasons for regarding the ergodic hypothesis in its original form as unsatisfactory, in spite of the fact that it leads to correct results. In recent years, therefore, a postulate known as the *hypothesis of equal a priori probabilities* for different regions in the phase space has been proposed. It is assumed that the probability of finding the phase point in any one region of phase space is identical with that for any other region of equal extension (or volume), provided the regions correspond equally well with the conditions that are known to apply to the system. (The word *probability* as used here means the fractional number of times a particular event is found to occur upon repeated trials of the same observation.) For example, if all that is known about the state of a system is that its energy lies between E and $E + \delta E$, then there will be equal probabilities of finding the representative (phase) point for the given system within equal volumes of the shell in γ -space corresponding to these energy limits. Further, if different extensions within this shell, having volumes v_1, v_2 , etc., are considered, the probability of the phase point for the system being in the respective regions will be proportional to these volumes.

Although the postulate enunciated in the preceding paragraph must be regarded as an assumption incapable of direct proof, it can be shown to be in reasonable harmony with the conclusions drawn from the Liouville theorem. A little consideration will show that the concept of equal a priori probabilities for different regions in the γ -space is compatible with the two principles concerning the conservation of density and the conservation of

extension in phase. According to the former of these principles, the density at a given phase point will remain unchanged as the point moves through the phase space. It follows, therefore, that there will be no tendency for phase points to collect in any particular region of the space. Further, the principle of the conservation of extension in phase means that once a particular volume (or extension) in phase space, containing a particular number of phase points, is defined, that volume will remain unchanged with the passage of time, although its shape may alter considerably. The constancy of the given volume with time and the lack of any tendency of phase points to concentrate in any region, suggest the reasonableness of the postulate that the probability of a representative point being in a given volume in the γ -space is proportional to that volume, provided, of course, that it lies in the region satisfying the known conditions as to energy, etc.

It will be seen later that the correspondence between volume in γ -space and the probability of finding the phase point for a given system, provides a useful means of bridging the gap between classical mechanics and the arguments of quantum mechanics. This may be regarded as a further advantage of the postulate of equal a priori probabilities over the older ergodic hypothesis.

47b. Systems of Similar Molecules.—For a system consisting of many molecules of the same kind, such as are of interest to the chemist, it is convenient to consider a space representation of all the coordinates and momenta, including those due to translation, vibration and rotation, of a single molecule, as distinct from that for the system as a whole. In order to distinguish them, the phase space, with $2f$ rectilinear axes, already used to represent a system, or ensemble of systems, has been called the γ -space, the letter γ standing for *gas*. The space employed for an individual molecule, or molecules, is then referred to as the μ -space, where μ is for *molecule*. Just as a representative point in γ -space indicates the precise state of a system, so a point in μ -space defines exactly the position and momentum of a single molecule. It is evident that the number of axes in μ -space will be less than those in the γ -space. If the molecule has r degrees of freedom, the μ -space will have $2r$ dimensions, and if there are n similar molecules in the system, the total number of degrees of freedom (f) will be equal to nr , and the number of dimensions in the γ -space ($2f$) is equal to $2nr$.

The state of each molecule in a system is determined by a representative point in its own $2r$ dimensional μ -space, and if there are *no appreciable forces* acting between the n molecules constituting the system, the state of the latter may be regarded as determined by a point in the γ -space obtained by combining the n individual μ -spaces. The location of a single representative point in the resulting γ -space will then give the exact position of each molecule in its own μ -space, and hence will give a precise specification of the state of the whole system.

In the application of statistical mechanics, a knowledge of the precise states of the molecules of a system is not so useful as specifications concerning the various small ranges within which the values of the coordinates and

momenta of the molecules might fall. In general, it may be supposed that the coordinates lie between q_1 and $q_1 + \delta q_1$, q_2 and $q_2 + \delta q_2$, etc., and the momenta lie between p_1 and $p_1 + \delta p_1$, p_2 and $p_2 + \delta p_2$, etc. It is convenient therefore, to consider the μ -space of a given molecule to be divided up into a number of elementary regions or *cells* of volume δv_μ , corresponding to the specified ranges in the q 's and p 's; thus,

$$\delta v_\mu = \delta q_1 \cdots \delta q_r \delta p_1 \cdots \delta p_r, \quad (47.1)$$

for the volume (or extension) in the $2r$ -dimensional μ -space. All the cells in the μ -space have equal extensions δv_μ , but their positions in the space will differ, corresponding to different values of the coordinates $q_1, \dots, q_r, p_1, \dots, p_r$ of the molecule. The particular cell in the μ -space may be identified by a subscript, viz., 1, 2, \dots , i , \dots , e.g., $(\delta v_\mu)_1, (\delta v_\mu)_2, \dots, (\delta v_\mu)_i$, etc., and if the cell in which the point representing a given molecule is situated is indicated by a letter, e.g., $(\delta v_\mu)_{1(a)}, (\delta v_\mu)_{2(b)}$, etc., the state of the molecule will be completely specified within the limits of the stipulated ranges of the coordinates and momenta.

In an exactly analogous manner, the γ -space may be divided up into cells of equal volume, corresponding to the ranges in the coordinates and momenta of the n constituent molecules. It is thus possible to represent the hypervolume δv_γ of a cell in the $2f$ -dimensional γ -space by the expression

$$\delta v_\gamma = (\delta v_\mu)_{1(a)} (\delta v_\mu)_{2(b)} \cdots (\delta v_\mu)_{i(j)} \cdots (\delta v_\mu)_{z(n)}, \quad (47.2)$$

where, in general, $(\delta v_\mu)_{i(j)}$ implies that the j th molecule occupies the i th cell in the μ -space. By specifying the particular cell in γ -space, as represented by equation (47.2), in which the phase point for the whole system is to be found, the state of the system is completely defined, for every molecule, within the postulated limits. Each molecule may lie in a different cell in the μ -space, but it is also possible for several molecules to occupy the same cell; this will occur if there are two molecules whose coordinates and momenta happen to fall within the same range. Interchange of the representative points of molecules within any one cell in the μ -space, does not change the identity of the cell in the γ -space. However, exchange of the phase points for molecules between different cells in the μ -space causes the system to move to a different cell in the γ -space. This implies that the molecules, although identical, can be distinguished from one another. Each arrangement of specified individual molecules having their representative points in particular cells in the μ -space is sometimes called a *microscopic state* or *complexion* of the system. It follows, therefore, that every microscopic state, or every complexion, of a given system occupies a different cell in the γ -space.

The *condition* or *macroscopic state* of a system of n molecules, as indicated by its observable properties, is determined by specifying the numbers, but not the identities, of the molecules whose representative points are to be found in the different unit cells in the μ -space. If these are identified, as

before, by the numerals $1, 2, \dots, i, \dots$, the number of representative points will be $n_1, n_2, \dots, n_i, \dots$, the total being equal to n . This means that there are n_1 molecules in the cell $(\delta v_\mu)_1$, with coordinates and momenta lying in the range $(q_1, \dots, q_r, p_1, \dots, p_r)_1$ and $(q_1 + \delta q_1, \dots, q_r + \delta q_r, p_1 + \delta p_1, \dots, p_r + \delta p_r)_1$; n_2 molecules in the cell $(\delta v_\mu)_2$ for the range $(q_1, \dots, q_r, p_1, \dots, p_r)_2$ and $(q_1 + \delta q_1, \dots, q_r + \delta q_r, p_1 + \delta p_1, \dots, p_r + \delta p_r)_2$; and, in general, n_i molecules in the cell $(\delta v_\mu)_i$ have coordinates and momenta in the range between $(q_1, \dots, q_r, p_1, \dots, p_r)_i$ and $(q_1 + \delta q_1, \dots, q_r + \delta q_r, p_1 + \delta p_1, \dots, p_r + \delta p_r)_i$. From the point of view of macroscopic properties and behavior of the system, it is immaterial which of the n similar molecules are taken as having representative points lying in the cells, specified by $1, 2, \dots, i, \dots$, in the μ -space. Hence, a large number of different unit cells in the γ -space, each having the volume δv_γ , as given by equation (47.2), will correspond to the same macroscopic state of the system. As seen above, the change from one cell in γ -space to another will arise from the exchange of representative points between the cells in the μ -space. The total number of unit cells in the γ -space that the phase point for the system as a whole can occupy, will be equal to the total number of microscopic states, or complexions, of the system. This number is found by considering the different possible ways of arranging a total of n *distinguishable* articles, so that there are n_1 in the first group, n_2 in the second, and so on, with, in general, n_i in the i th group; this is given by

$$G = \frac{n!}{n_1! n_2! \dots n_i! \dots}, \quad (47.3)$$

and hence there are G unit cells in the γ -space all corresponding to the same macroscopic state. Since the unit cells have equal volumes, the quantity G gives the total volume in the γ -space occupied by the representative points of the system under consideration.

THE CLASSICAL DISTRIBUTION LAW

48a. The Maxwell-Boltzmann Distribution Law.—Consider a system made up of a large number of similar molecules enclosed in a vessel of constant volume. Suppose all that is known about the system is that its energy E is constant; it is then convenient to use the methods of statistical mechanics to obtain further information as to the most probable behavior of the system. For this purpose it is necessary, as mentioned previously, to choose an appropriate ensemble of similar systems, and to consider their behavior. A particular ensemble that is especially suitable for the type of system postulated is the microcanonical ensemble. In this case the points representing the systems are distributed uniformly through a thin shell lying between two surfaces in the γ -space representing constant energies of E and $E + \delta E$, respectively. By permitting δE to approach zero, the uniformity of distribution is still maintained, while the energy of every system approaches the required constant value E . It will be remembered that the

microcanonical ensemble is in statistical equilibrium; hence, the results obtained by its aid apply to equilibrium conditions, which do not change with time.

The uniformity of distribution, independent of time, of representative points throughout the specified region in γ -space, that is characteristic of the microcanonical ensemble, is evidently compatible with the postulate of equal a priori probabilities in phase space. Suppose the system of n similar, but distinguishable, molecules considered in the preceding section has a total energy which lies within the range of E to $E + \delta E$; it follows, then, from the aforementioned postulate, that the probability of finding the system in the state in which n_1 molecules are in the first cell, n_2 in the second cell, and so on, with n_i in the i th cell, is proportional to G , the number of unit cells, i.e., the total volume, occupied by the system in the γ -space; thus,

$$W = \frac{n!}{n_1! n_2! \dots n_i! \dots} \times \text{constant}, \quad (48.1)$$

where W is the required probability. It may be remarked that the proportionality constant, which relates the probability (W) of the particular system to the volume (G) its representative points occupy in phase space, has the same value for any macroscopic state of the system.

The most probable distribution of molecules among the cells in the μ -space, that is to say, with coordinates and momenta lying in specified ranges, is found by investigating the conditions which make the probability W , as given by equation (48.1), have a maximum value. For this purpose, it is convenient to express the condition of maximum probability in the form

$$\delta \ln W = 0. \quad (48.2)$$

Upon taking logarithms of equation (48.1), it is seen that

$$\ln W = \ln n! - \sum_i \ln n_i! + \text{constant}, \quad (48.3)$$

but this expression can be simplified by making use of Stirling's formula for the factorials of large numbers, viz.,

$$\ln n! = (n + \frac{1}{2}) \ln n - n + \frac{1}{2} \ln 2\pi + \dots \quad (48.4)$$

Since n is large, $n + \frac{1}{2}$ may be replaced by n ; further the term $\frac{1}{2} \log 2\pi$ and those beyond may be neglected, giving

$$\ln n! = n \ln n - n. \quad (48.4)$$

In systems of practical interest the total number n of molecules is very large; further, it may be supposed that most of the numbers n_i , for the molecules in the various cells in μ -space, are also large, so that the simplified Stirling formula, equation (48.4), may be used for all the factorials in equation

(48.3). The latter then becomes

$$\begin{aligned}\ln W &= n \ln n - n - \sum_i (n_i \ln n_i - n_i) + \text{constant} \\ &= n \ln n - \sum_i n_i \ln n_i + \text{constant},\end{aligned}\quad (48.5)$$

remembering that $\sum n_i$ is equal to n . Differentiation of equation (48.5) gives

$$\begin{aligned}\delta \ln W &= - \sum_i \delta(n_i \ln n_i) \\ &= - \sum_i (\ln n_i + 1) \delta n_i,\end{aligned}\quad (48.6)$$

and upon introduction of equation (48.2), the condition for the maximum probability is seen to be

$$\sum_i (\ln n_i + 1) \delta n_i = 0. \quad (48.7)$$

In connection with the further examination of this equation, it is necessary to recall certain restrictions which apply to the system under consideration. Since the total number of molecules n is constant, it follows that the variations δn_i in the numbers n_i in the various cells in μ -space are not completely arbitrary, but must always add up to zero; thus, since

$$\sum_i n_i = n = \text{constant},$$

it follows that

$$\sum_i \delta n_i = \delta n = 0. \quad (48.8)$$

Further, it has been postulated that the energy of the system remains constant, within the small range required to specify the microcanonical ensemble. The molecules in each particular cell in the μ -space will have a definite energy within the small range over which the coordinates can vary in the unit cell. If ϵ_i , in the general case, is the energy of a molecule in the i th cell,² and E is the constant total energy of the system, then

$$\sum_i \epsilon_i n_i = E = \text{constant},$$

and hence

$$\sum_i \epsilon_i \delta n_i = \delta E = 0. \quad (48.9)$$

The equations (48.7), (48.8) and (48.9) represent the conditions which must be satisfied simultaneously for the system of maximum probability. Using the Lagrange method of undetermined multipliers, that is, on multi-

² Strictly speaking ϵ_i should be defined by $\partial E / \partial n_i$, like a partial molar quantity, i.e., the rate of increase in energy of the system per molecule added to the i th cell at equilibrium. If the system behaves ideally, however, and there is no interaction between the molecules, ϵ_i may be identified with the actual energy per molecule.

plying equations (48.8) and (48.9) by the undetermined constants α and β , respectively, and adding to equation (48.7), the result is

$$\sum_i (\ln n_i + 1 + \alpha + \beta \epsilon_i) \delta n_i = 0. \quad (48.10)$$

The integer 1 in equation (48.10) may be combined with α to give a new constant which for convenience, may also be represented by α , so that the equation may be written as

$$\sum_i (\ln n_i + \alpha + \beta \epsilon_i) \delta n_i = 0. \quad (48.11)$$

Since the variations δn_i in the cells in the μ -space are independent of each other, with the restrictions already included in equations (48.8) and (48.9), it will be seen that equation (48.11) will be satisfied, in general, only if each term in the summation is zero; thus

$$\begin{aligned} \ln n_i + \alpha + \beta \epsilon_i &= 0, \\ \therefore \ln n_i &= -(\alpha + \beta \epsilon_i), \end{aligned}$$

for every cell i in the μ -space. This equation may be put in the form

$$n_i = e^{-(\alpha + \beta \epsilon_i)} \quad (48.12)$$

or

$$n_i = \frac{1}{e^{\alpha + \beta \epsilon_i}}. \quad (48.13)$$

The result represented by equation (48.12) or (48.13) is of fundamental importance to classical statistical mechanics; it is a form of what is known as the *Maxwell-Boltzmann distribution law*. These equations give the most probable distribution of molecules among the various possible individual energy values, at statistical equilibrium, for a system of constant total energy. It may be mentioned that it is possible to show by the theory of fluctuations, itself an aspect of statistical mechanics, that provided the total number of molecules in a system is large, as is almost invariably true, the most probable distribution, as given by equation (48.12) or (48.13), is very much more probable than any other distribution that differs from it to any appreciable extent. It follows, therefore, that equation (48.12) or (48.13) may be regarded as representing the actual behavior of a system involving a large number of molecules. Attention may be called to the fact that in deriving the Maxwell-Boltzmann distribution law, no restriction was made as to the nature of the energy, i.e., translational vibrational, rotational, etc. The equations may thus be regarded as applicable to the distribution of the total energy or of any form of energy which has a constant value for the given system.

Before proceeding to the further development of the Maxwell-Boltzmann law, it is desirable to call attention to the approximations and assumptions

made in its derivation. In the first place, it has been assumed that the molecules are distinguishable; this aspect of the subject will be taken up more fully later in connection with a discussion of quantum statistics. Secondly, the use of the Stirling approximation for $n_i!$ presupposes that all the n_i values are very large. Finally, the tacit assumption has been made that both n_i and ϵ_i are continuously variable; this is not serious provided n_i is always large and the energy quanta are small, as is particularly the case for translational energy. The general validity of the distribution law, as far as classical mechanics is concerned, is established by the fact that it is possible to derive exactly the same equation by methods which do not involve the approximations made here. It must be remembered, of course, that in every case the identification of ϵ_i with the actual energy of a molecule in the i th cell in the μ -space presupposes the absence of forces acting between the molecules. The systems are thus assumed to consist of ideal gases, for it is only in these circumstances that intermolecular forces are completely absent. However, under such conditions that the deviations from ideal behavior are not large, the Maxwell-Boltzmann distribution law may be employed without incurring serious error.

48b. Evaluation of the Maxwell-Boltzmann Constants.—The Maxwell-Boltzmann distribution law may be written in a form which calls attention to the relationship between the number of molecules in any region of the μ -space, and the volume (or extension) of that region. A constant C is defined in terms of the constant α that appears in equation (48.12); thus,

$$e^{-\alpha} = nC\delta q_1 \cdots \delta q_r \delta p_1 \cdots \delta p_r, \quad (48.14)$$

where, as before, n is the total number of molecules and $\delta q_1 \cdots \delta q_r \delta p_1 \cdots \delta p_r$, later abbreviated to $\delta q_1 \cdots \delta p_r$, is the volume in the μ -space of the unit cells into which this space has been divided. The expression for $e^{-\alpha}$ may be substituted into equation (48.12), and at the same time n_i , the number of molecules in the i th unit cell, may be replaced by δn , while the subscript is eliminated from ϵ_i ; the Maxwell-Boltzmann equation then takes the differential form

$$\delta n = nC e^{-\beta \epsilon} \delta q_1 \cdots \delta p_r. \quad (48.15)$$

This result shows that the number of molecules δn in any unit cell of the μ -space is proportional to the volume $\delta q_1 \cdots \delta p_r$ of that cell, as determined by the corresponding postulated ranges of the momenta and coordinates.

If equation (48.15) is integrated over all possible values of the coordinates and momenta that any molecule may possess, the result must be equal to the total number of molecules n , so that

$$n = \int_0^n dn = nC \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} e^{-\beta \epsilon} dq_1 \cdots dp_r, \quad (48.16)$$

the limits of the $2r$ integrals being from $-\infty$ to ∞ for all the q 's and p 's.

From this it is seen that

$$\frac{1}{C} = \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} e^{-\beta \epsilon} dq_1 \cdots dp_r. \quad (48.17)$$

In order to evaluate the constant C (or α and β), it is convenient to consider a system involving a dilute monatomic gas, which may be regarded as exhibiting ideal behavior, contained in a vessel of volume v . Molecules of this type may be treated as point particles; the position of each molecule will then be given by three cartesian coordinates x, y, z , and the corresponding momenta p_x, p_y, p_z . For this system, equation (48.17) then takes the form

$$\frac{1}{C} = \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} e^{-\beta \epsilon} dx dy dz dp_x dp_y dp_z. \quad (48.18)$$

Integration over the coordinates x, y, z , gives the volume v of the containing vessel, i.e.,

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dx dy dz = v, \quad (48.19)$$

so that

$$\frac{1}{C} = v \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-\beta \epsilon} dp_x dp_y dp_z. \quad (48.20)$$

Since the system has been assumed to consist of an ideal monatomic gas, ϵ may be identified with the kinetic energy per molecule, and this may be written as

$$\epsilon = \frac{1}{2m} (p_x^2 + p_y^2 + p_z^2). \quad (48.21)$$

The three components p_x, p_y, p_z of the momentum of the molecule are independent; hence equation (48.21) may be introduced into (48.20), and the variables separated to give

$$\frac{1}{C} = v \int_{-\infty}^{\infty} e^{-\beta p_x^2/2m} dp_x \int_{-\infty}^{\infty} e^{-\beta p_y^2/2m} dp_y \int_{-\infty}^{\infty} e^{-\beta p_z^2/2m} dp_z. \quad (48.22)$$

The three integrals are of the standard form

$$\int_{-\infty}^{\infty} e^{-ax^2} dx = \left(\frac{\pi}{a} \right)^{1/2}, \quad (48.23)$$

and hence it follows that

$$\frac{1}{C} = v \left(\frac{2\pi m}{\beta} \right)^{3/2}. \quad (48.24)$$

The total energy E of the n molecules may be expressed by the relationship

$$E = \int_0^n \epsilon dn, \quad (48.25)$$

and utilizing equation (48.15), which in the case under consideration may be written as

$$dn = nC e^{-\beta \epsilon} dx dy dz dp_x dp_y dp_z, \quad (48.26)$$

it follows that

$$E = nC \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \epsilon e^{-\beta \epsilon} dx dy dz dp_x dp_y dp_z, \quad (48.27)$$

Making use, as before, of the fact that integration over the coordinates x, y, z , gives the volume v , and then introducing equation (48.21) for ϵ , equation (48.27) becomes

$$E = \frac{nvC}{2m} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} (p_x^2 + p_y^2 + p_z^2) e^{-(p_x^2 + p_y^2 + p_z^2)/2m} dp_x dp_y dp_z. \quad (48.28)$$

Since the variables p_x, p_y and p_z are independent, the triple integral is readily seen to be equal to the sum of three equivalent expressions of the form

$$I = \int_{-\infty}^{\infty} p_x^2 e^{-p_x^2/2m} dp_x \int_{-\infty}^{\infty} e^{-p_y^2/2m} dp_y \int_{-\infty}^{\infty} e^{-p_z^2/2m} dp_z. \quad (48.29)$$

Utilizing the standard integral

$$\int_{-\infty}^{\infty} x^2 e^{-ax^2} dx = \frac{1}{2} \left(\frac{\pi}{a} \right)^{1/2}, \quad (48.30)$$

together with the standard integral in equation (48.23), the value of I in equation (48.29) becomes

$$I = \frac{m}{\beta} \left(\frac{2\pi m}{\beta} \right)^{3/2}. \quad (48.31)$$

The three integrals of (48.28) are each equal to I , given by equation (48.31), so that

$$E = \frac{nvC}{2m} \cdot \frac{3m}{\beta} \left(\frac{2\pi m}{\beta} \right)^{3/2},$$

and if the value of C given by equation (48.24) is introduced, it is found that

$$E = \frac{3n}{2\beta}. \quad (48.32)$$

For one mole of gas, the number of molecules n will be equal to the Avogadro number N , and hence for one mole,

$$E = \frac{3N}{2\beta}. \quad (48.33)$$

For one mole of an ideal monatomic gas, it is to be expected, e.g., from heat capacity determinations, that

$$\begin{aligned} E &= \frac{3}{2}RT \\ &= \frac{3}{2}NkT, \end{aligned} \quad (48.34)$$

where k , equal to R/N , is the gas constant per single molecule, generally known as the *Boltzmann constant*. Comparison of equations (48.33) and (48.34) shows that

$$\beta = \frac{1}{kT}, \quad (48.35)$$

so that this is the value of β for a monatomic gas; it will be proved below that it has the same value for any gas satisfying the Maxwell-Boltzmann law. Combination of equation (48.35) with (48.24) gives for a monatomic molecule

$$\frac{1}{C} = (2\pi mkT)^{3/2}v. \quad (48.36)$$

48c. Mixtures of Gases.—In the preceding section the value of β was determined for the special case of a monatomic ideal gas, but there is no certainty that the result obtained will be applicable to other cases. It is true that there is nothing in equation (48.35) that has any reference to the properties of the substance involved, but it would be desirable if a more definite proof were available that β was independent of the nature of the gas molecules. Such proof can be obtained by considering a mixture of n, n', n'', \dots molecules of different gases; let n_i, n'_j, n''_k, \dots be the numbers of the respective molecules required to occupy the various equal cells i, j, k, \dots , into which the μ -spaces for the different kinds of molecules are divided. The probability W of finding the system in the specified state when statistical equilibrium is attained is then given by

$$W = \frac{n!}{n_1! \dots n_i! \dots} \cdot \frac{n'!}{n'_1! \dots n'_j! \dots} \cdot \frac{n''!}{n''_1! \dots n''_k! \dots} \dots \times \text{constant}, \quad (48.37)$$

and hence, after introducing the Stirling approximation,

$$\ln W = (n \ln n - \sum_i n_i \ln n_i) + (n' \ln n' - \sum_j n'_j \ln n'_j) + \cdots + \text{constant.} \quad (48.38)$$

The condition for the maximum probability is then

$$\sum_i (\ln n_i + 1) \delta n_i + \sum_j (\ln n'_j + 1) \delta n'_j + \cdots = 0. \quad (48.39)$$

Since the total number of each kind of molecular species remains constant,

$$\sum_i \delta n_i = 0, \quad (48.40)$$

$$\sum_j \delta n'_j = 0. \quad (48.41)$$

...

Further, the *total* energy of the system has a definite value, and hence

$$\sum_i \epsilon_i \delta n_i + \sum_j \epsilon'_j \delta n'_j + \cdots = 0. \quad (48.42)$$

Multiplying equations (48.40), (48.41), ..., by α , α' , ..., respectively, and equation (48.2) by β , and adding the result to equation (48.39), according to the method of undetermined multipliers, it is found that

$$\sum_i (\ln n_i + \alpha + \beta \epsilon_i) \delta n_i + \sum_j (\ln n'_j + \alpha' + \beta \epsilon'_j) \delta n'_j + \cdots = 0. \quad (48.43)$$

The variations δn among the different gases can be treated as independent, and the result, analogous to equation (48.12) for a single species, is

$$n_i = e^{-(\alpha + \beta \epsilon_i)} \quad (48.44)$$

$$n'_j = e^{-(\alpha' + \beta \epsilon'_j)} \quad (48.45)$$

...

It is apparent that although the constant α varies from one kind of molecule to another, β is the same throughout; the reason for this is seen to lie in the fact that the number of *each kind* of molecule is constant, whereas for the energy it is the total energy for *all* the molecules that is unchanged.

Suppose that one of the constituents of a mixture of two or more ideal gases is a monatomic substance; when statistical and temperature equilibrium is attained, the value of β in the equation giving the distribution of the molecules of the monatomic gas is equal to $1/kT$, as already shown. From the arguments just presented it is apparent that this will be the same in the equations (48.44), (48.45), etc., for the distribution of the molecules of the other gases. It follows, therefore, that the value of β in the Maxwell-

Boltzmann equation is always equal to $1/kT$, irrespective of the nature of the molecules concerned.

It will be noted from equation (48.36) that C is not independent of the gas, as it involves the mass m of the molecules. Since α is related to C by means of equation (48.14), it is evident, as is to be expected from the foregoing arguments, that α will vary from one substance to another.

49a. Maxwell's Law of Distribution of Velocities.—The special form of the distribution law applicable to the velocities, or kinetic energies, of molecules was first derived by Maxwell by means of the kinetic theory of gases. It can be obtained readily from one of the general forms of the Maxwell-Boltzmann distribution law, in the following manner. Since the components of translational energy are the only properties of interest for the present problem, any molecule may be regarded as behaving like a monatomic molecule, provided the translational energy can be treated as separable from the other (internal) forms of energy (cf. Section 57a); this is probably justifiable in a constant, or zero, force field. Under these circumstances, the distribution law equation (48.15) is equivalent to equation (48.26); introducing the value for β , equal to $1/kT$, the latter equation becomes

$$dn = nC e^{-1/kT} dx dy dz dp_x dp_y dp_z, \quad (49.1)$$

where C has the value given by equation (48.36) for a monatomic molecule. Equation (49.1) may now be integrated over the coordinates x, y, z , as before, to give v ; the resulting expression, after introduction of (48.36), is

$$dn = \frac{n}{(2\pi mkT)^{3/2}} e^{-1/kT} dp_x dp_y dp_z, \quad (49.2)$$

which holds for all the molecules in the given containing vessel.

The kinetic (translational) energy ϵ may now be replaced by

$$\epsilon = \frac{1}{2}m(\dot{x}^2 + \dot{y}^2 + \dot{z}^2), \quad (49.3)$$

and at the same time the momenta may be written in the form $p_x = m\dot{x}$, etc., so that

$$dp_x = m d\dot{x}, \quad dp_y = m d\dot{y}, \quad \text{and} \quad dp_z = m d\dot{z}. \quad (49.4)$$

With these changes in the variables, equation (49.2) becomes

$$dn = n \left(\frac{m}{2\pi kT} \right)^{3/2} e^{-m(\dot{x}^2 + \dot{y}^2 + \dot{z}^2)/2kT} d\dot{x} d\dot{y} d\dot{z}, \quad (49.5)$$

which is the form of the Maxwell distribution law for the number of molecules having components of velocity in the range \dot{x} to $\dot{x} + d\dot{x}$, \dot{y} to $\dot{y} + d\dot{y}$, and \dot{z} to $\dot{z} + d\dot{z}$.

The resultant speed of translation c of a molecule is given by

$$c^2 = \dot{x}^2 + \dot{y}^2 + \dot{z}^2, \quad (49.6)$$

and, in terms of polar coordinates,

$$dxdydz = c^2 \sin \theta d\theta d\phi dc. \quad (49.7)$$

Changing the variables, equation (49.5) takes the form

$$dn = n \left(\frac{m}{2\pi kT} \right)^{3/2} e^{-mc^2/2kT} c^2 \sin \theta d\theta d\phi dc. \quad (49.8)$$

This expression gives the number of molecules with speeds between c and $c + dc$, in a direction lying within the angular range θ to $\theta + d\theta$, and ϕ to $\phi + d\phi$. In order to obtain the number of molecules having velocities between c and $c + dc$ irrespective of direction, it is necessary to integrate equation (49.8) with respect to θ , between the limits of zero and π , and with respect to ϕ , between the limits of zero and 2π , thus including all possible directions; hence,

$$\begin{aligned} dn &= n \left(\frac{m}{2\pi kT} \right)^{3/2} e^{-mc^2/2kT} c^2 dc \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi \\ &= 4\pi n \left(\frac{m}{2\pi kT} \right)^{3/2} e^{-mc^2/2kT} c^2 dc. \end{aligned} \quad (49.9)$$

Since the kinetic energy ϵ is also equal to $\frac{1}{2}mc^2$, i.e.,

$$\frac{1}{2}mc^2 = \epsilon,$$

it is readily shown that

$$c^2 dc = \frac{(2\epsilon)^{1/2}}{m^{3/2}} d\epsilon,$$

and hence equation (49.9) may be written as

$$dn = \frac{2\pi n}{(\pi kT)^{3/2}} e^{-\epsilon/kT} \epsilon^{1/2} d\epsilon. \quad (49.10)$$

This gives the number of molecules with kinetic (translational) energy lying between ϵ and $\epsilon + d\epsilon$ in any direction.

49b. Mean Values in Statistical Mechanics.—The Maxwell-Boltzmann equation (48.12) gives the distribution of molecules having specified momenta and coordinates, lying within certain limits; consequently the equation may be employed to calculate the mean value of any function of these variables, e.g., velocity or energy. The procedure is to take the fraction of the molecules having a particular value of the given property, to multiply it by this value, and then to sum (or integrate) over all the molecules. Since equation (48.15) gives the number of molecules having coordinates and momenta within a specified range, the fraction of the total number n of molecules having these coordinates and momenta is obtained on dividing

by n ; thus

$$\frac{dn}{n} = Ce^{-\epsilon/kT} dq_1 \cdots dp_r, \quad (49.11)$$

in which β has been replaced by its known value $1/kT$. If R is any property that is a function of the coordinates and momenta, the mean value of R , represented by \bar{R} , is then given by

$$\bar{R} = C \int \cdots \int R e^{-\epsilon/kT} dq_1 \cdots dp_r.$$

Introducing the expression for C , given by equation (48.17), it follows that

$$\bar{R} = \frac{\int \cdots \int R e^{-\epsilon/kT} dq_1 \cdots dp_r}{\int \cdots \int e^{-\epsilon/kT} dq_1 \cdots dp_r}. \quad (49.12)$$

The use of this equation may be illustrated by calculating the mean velocity \bar{c} , irrespective of direction, of the molecules of an ideal gas; this may be written in the most general form as

$$\bar{c} = \frac{\int \cdots \int c e^{-\epsilon/kT} dx dy dz dp_x dp_y dp_z}{\int \cdots \int e^{-\epsilon/kT} dx dy dz dp_x dp_y dp_z}. \quad (49.13)$$

Since ϵ is independent of the coordinates x, y, z , these may be integrated out from numerator and denominator of equation (49.13); at the same time the variables may be changed by means of the equations (49.4), with the result

$$\bar{c} = \frac{\iiint c e^{-\epsilon/kT} d\dot{x} d\dot{y} d\dot{z}}{\iiint e^{-\epsilon/kT} d\dot{x} d\dot{y} d\dot{z}}. \quad (49.14)$$

As in Section 49a, conversion is made to polar coordinates; at the same time ϵ may be replaced by $\frac{1}{2}mc^2$, so that

$$\begin{aligned} \bar{c} &= \frac{\int_0^\pi \int_0^{2\pi} \int_0^\infty c^3 e^{-mc^2/2kT} \sin \theta d\theta d\phi dc}{\int_0^\pi \int_0^{2\pi} \int_0^\infty c^2 e^{-mc^2/2kT} \sin \theta d\theta d\phi dc} \\ &= \frac{\int_0^\infty c^3 e^{-mc^2/2kT} dc}{\int_0^\infty c^2 e^{-mc^2/2kT} dc}. \end{aligned}$$

Since there is no restriction as to the direction of c , its value can vary from zero to infinity; these are, therefore, the limits of integration. The integrals in both numerator and denominator are standard forms; thus,

$$\bar{c} = \frac{\frac{1}{2} \left(\frac{2kT}{m} \right)^2}{\frac{\pi^{1/2}}{4} \left(\frac{2kT}{m} \right)^{3/2}} = \left(\frac{8kT}{\pi m} \right)^{1/2}. \quad (49.15)$$

This result gives the mean speed of the molecules regardless of direction; for certain purposes it is desirable to know the mean value of the component of velocity in a particular direction; if this is in *one* direction, parallel to the x axis, equation (49.14) becomes

$$\bar{\dot{x}} = \frac{\int_0^\infty \dot{x} e^{-m\dot{x}^2/2kT} d\dot{x}}{\int_{-\infty}^\infty e^{-m\dot{x}^2/2kT} d\dot{x}},$$

where the energy ϵ is now $\frac{1}{2}m\dot{x}^2$. The integration in the numerator is from zero to infinity, but in the denominator the limits are $-\infty$ to ∞ , to allow for the fact that molecules can move in *both* directions parallel to the same axis. Utilizing the standard integrals, it is found that

$$\bar{\dot{x}} = \frac{\frac{kT}{m}}{\left(\frac{2\pi kT}{m} \right)^{1/2}} = \left(\frac{kT}{2\pi m} \right)^{1/2}. \quad (49.16)$$

49c. Principle of the Equipartition of Energy.—The average energy of the molecules in a given system is represented by

$$\bar{\epsilon} = \frac{\int \cdots \int \epsilon e^{-\epsilon/kT} dq_1 \cdots dp_r}{\int \cdots \int e^{-\epsilon/kT} dq_1 \cdots dp_r}, \quad (49.17)$$

and this could be evaluated if the dependence of the energy on the coordinates and momenta were known. The treatment can be simplified when the energy components corresponding to one or more of the variables, i.e., the coordinates and momenta, are separable from the others. For example, if the energy $\epsilon(p_i)$ associated with the momentum p_i may be treated as independent of the other forms of energy $\epsilon(p, q)$, then it is possible to write

$$\epsilon = \epsilon(p_i) + \epsilon(p, q),$$

and hence

$$\bar{\epsilon}(p_i) = \frac{\int \cdots \int \epsilon(p_i) e^{-\epsilon/kT} dq_1 \cdots dp_r}{\int \cdots \int e^{-\epsilon/kT} dq_1 \cdots dp_r} \quad (49.18)$$

$$= \frac{\int \cdots \int \epsilon(p_i) e^{-\epsilon(p_i)/kT} e^{-\epsilon(p,q)/kT} dq_1 \cdots dp_r}{\int \cdots \int e^{-\epsilon(p_i)/kT} e^{-\epsilon(p,q)/kT} dq_1 \cdots dp_r}. \quad (49.19)$$

Since $\epsilon(p_i)$ and $e^{-\epsilon(p_i)/kT}$ depend only on the variable p_i , all the other variables can be integrated out, the result being the same for both numerator and denominator; equation (49.19) then becomes

$$\bar{\epsilon}(p_i) = \frac{\int \epsilon(p_i) e^{-\epsilon(p_i)/kT} dp_i}{\int e^{-\epsilon(p_i)/kT} dp_i}. \quad (49.20)$$

If the energy can be expressed as a quadratic function of p_i , viz.,

$$\epsilon(p_i) = ap_i^2, \quad (49.21)$$

where a is a constant, it follows that

$$\begin{aligned} \bar{\epsilon}(p_i) &= \frac{\int_{-\infty}^{\infty} ap_i^2 e^{-ap_i^2/kT} dp_i}{\int_{-\infty}^{\infty} e^{-ap_i^2/kT} dp_i} \\ &= \frac{1}{2}kT. \end{aligned} \quad (49.22)$$

Exactly the same result, i.e., $\frac{1}{2}kT$, would have been obtained for the mean value if the energy had been a quadratic function of one of the coordinates e.g., $\epsilon(q_i)$. It follows, therefore, that the average energy associated with each single variable, coordinate or momentum, which contributes a *quadratic term* (or *square term*) to the total energy, is $\frac{1}{2}kT$ per molecule in every case. This conclusion is generally referred to as the *principle of the equipartition of energy*.

The component of the kinetic energy of a molecule in any direction may be expressed as a quadratic function of the corresponding momentum, e.g., $\epsilon_i = p_i^2/2m$; hence the mean value of the kinetic energy per molecule in that direction is $\frac{1}{2}kT$. For a monatomic gas, the total energy is kinetic in nature and is made up of three components corresponding to three momenta; the energy is thus $\frac{3}{2}kT$ per molecule, or $\frac{3}{2}NkT$, i.e., $\frac{3}{2}RT$, per mole. This result was, of course, used in the proof that β is equal to $1/kT$, but the conclusions

are independent of this fact because the same value for β may be derived in other ways; one of these will be indicated below.

The energy ϵ_r of a rotator is entirely kinetic in character; for each type of rotation,

$$\epsilon_r = \frac{p_\theta^2}{2I}, \quad (49.23)$$

where p_θ is the angular momentum and I is the moment of inertia about the axis of rotation. The rotational energy is thus a quadratic function of the corresponding momentum; every type of rotation of the molecule as a whole will thus contribute $\frac{1}{2}kT$ per molecule, or $\frac{1}{2}RT$ per mole, to the total energy.

The energy ϵ_v of a linear harmonic oscillator is given by the sum of two square terms, one involving a momentum p , and the other a coordinate q ; thus

$$\epsilon_v = \frac{p^2}{2m} + \frac{1}{2}fq^2, \quad (49.24)$$

where the first term on the right-hand side is the vibrational kinetic energy and the second term is the potential energy. It follows, therefore, that the average energy of the oscillator will be twice $\frac{1}{2}kT$, i.e., kT , per molecule, or RT per mole.

In general, for a nonlinear molecule containing n atoms, there are three components of translational energy, three rotations and $3n - 6$ vibrational modes; the total energy per mole, according to the equipartition principle, should thus be $(3n - 3)RT$. Utilizing the thermodynamic expression $(\partial E/\partial T)_V$ for the heat capacity at constant volume, the latter should be $(3n - 3)R$ for a nonlinear n -atomic molecule. Experiments show, however, that this value is attained only at high temperatures; at lower temperatures the heat capacities are less than the results derived from the principle of the equipartition of energy. This principle is thus an approximation; the reason will be seen later to be due to the neglect of the quantization of energy.

Apart from the assumptions involved in the foregoing (classical) treatment, that the intermolecular forces are negligible and that the different forms of the energy are separable, it must be emphasized that the equipartition principle depends on the particular form of the energy being an exact quadratic function of the corresponding coordinate or momentum [cf. equation (49.21)]. If this is not the case, the principle must inevitably fail, even at high temperatures. For example, if the linear oscillations are not strictly harmonic in character, the potential energy will not be given by $\frac{1}{2}fq^2$, but by an expression of the form (cf. Section 29b)

$$\epsilon = \frac{1}{2}fq^2 + aq^3 + bq^4 + \dots$$

It is obvious that in this case the average energy corresponding to the particular coordinate q will not be equal to $\frac{1}{2}kT$ per molecule.

49d. Calculation of Gas Pressure.—Consider a rectangular box of volume v containing n molecules; the pressure on the walls of the box is due

to the bombardment of the molecules which are moving in all directions. Since no direction is preferred over any other, the pressure on any one face of the box, e.g., that perpendicular to the x axis, which will be the same as that on the others, may be regarded as due to the x component of the velocities of all the molecules. If \bar{x} is the mean velocity component in the x direction, the change of momentum resulting from the impact of a single molecule under consideration is $2m\bar{x}$, where m is the mass of the molecule. All molecules within a distance \bar{x} should reach each square centimeter of the wall in unit time. Since there are n molecules in the volume v , it follows that $n\bar{x}/v$ molecules strike the wall in unit time. The rate of change of momentum per sq. cm. of wall is thus $2mn\bar{x}^2/v$, and this, by definition, must equal the pressure P exerted by the molecules; thus,

$$P = \frac{2mn\bar{x}^2}{v}. \quad (49.25)$$

The value of \bar{x}^2 may be derived in a manner exactly analogous to that employed in Section 49b to determine \bar{x} ; thus

$$\bar{x}^2 = \frac{\int_0^\infty x^2 e^{-m\dot{x}^2/2kT} d\dot{x}}{\int_{-\infty}^\infty e^{-m\dot{x}^2/2kT} d\dot{x}} = \frac{kT}{2m}. \quad (49.26)$$

Insertion of this result into equation (49.25) then gives

$$P = \frac{nkT}{v}.$$

If N is the number of molecules in 1 mole, and V is the corresponding volume, it follows that

$$P = \frac{NkT}{V} = \frac{RT}{V}, \quad (49.27)$$

which is the equation of state for an ideal gas. This result is, of course, to be expected, since the Maxwell-Boltzmann equation, upon which (49.26) is based, is applicable when there are no intermolecular forces. It may be noted, incidentally, that by assuming the result of equation (49.27) it is possible to derive the value $1/kT$ for the constant β .

QUANTUM STATISTICS

50a. Indistinguishability of Similar Particles.—In the foregoing sections the treatment has been based on classical concepts; for example, it is tacitly assumed that it is possible to define exactly both the position (coordinate) and velocity (momentum) of a molecule. It is desirable to consider now what changes, if any, have to be made in the results obtained by classical statistical mechanics as a consequence of the application of the modern

ideas of quantum theory and wave mechanics. It has been repeatedly mentioned that the derivation of the Maxwell-Boltzmann equation involved the postulate that molecules of a particular species, in spite of being similar, were distinguishable from one another. It was supposed that if two molecules, or other particles, whose representative points occupied different unit volumes in the μ -space were interchanged, there resulted a new microscopic state. This supposition implies, in principle, that during the process of molecular interchange it is possible to keep both molecules under precise observation during the whole time, without producing any disturbing effect on them. However, according to the Heisenberg uncertainty principle (cf. Section 3b), it is not possible to maintain exact observation on the states of the molecules without affecting the system in some manner. In other words, although it may be possible classically to determine whether two molecules in different cells in the μ -space have interchanged, the possibility is forbidden by quantum mechanics. Consequently, in quantum statistics two or more states that cannot be distinguished from one another by conceivable observations are to be regarded as being merely one state.

The same conclusion may be reached in a somewhat more precise manner by means of some elementary arguments of quantum mechanics. Consider two exactly similar particles, whose coordinates are q_1 and q_2 , respectively. Suppose there are two eigenfunctions u_a and u_b available, so that the solutions of the wave equation for the two separated particles would be either $u_a(q_1)$ and $u_b(q_2)$, or $u_a(q_2)$ and $u_b(q_1)$. Since the two particles are entirely similar, it is evident, as in the case of the hydrogen molecule discussed in Section 15, that there will be two possible solutions of the Schrödinger equation for the system as a whole; these are the symmetric eigenfunction

$$\psi_s = \frac{1}{\sqrt{2}} \{ u_a(q_1)u_b(q_2) + u_a(q_2)u_b(q_1) \}$$

and the antisymmetric function

$$\psi_A = \frac{1}{\sqrt{2}} \{ u_a(q_1)u_b(q_2) - u_a(q_2)u_b(q_1) \},$$

where $1/\sqrt{2}$ is the normalizing factor in each case.

According to the wave mechanics, the average value of any property is given by the expression

$$\bar{R} = \int R\psi^*\psi d\tau,$$

where $\psi^*\psi$ is the probability distribution function (Section 5a). In the present case, therefore, the symmetric and antisymmetric eigenfunctions lead to the following results

$$\bar{R}_s = \int R\psi_s^*\psi_s d\tau$$

and

$$\bar{R}_A = \int R \psi_A^* \psi_A d\tau.$$

It should now be observed that in the case of the symmetric solution, an exchange of the coordinates of the particles leaves both ψ_S^* and ψ_S unchanged; the mean value of the property R is consequently unaffected by the exchange. For the antisymmetric case, an exchange of coordinates alters the signs of both ψ_A^* and ψ_A , with the result that \bar{R}_A is again unchanged. Any interchange of the two particles thus leaves the observed property of the system completely unaffected. In other words, wave mechanics denies the possibility of distinguishing between the two similar particles, so that the classical statistics of Boltzmann must be abandoned in favor of alternative schemes. Two forms of quantum statistics, applicable to particles of different types, have been proposed; the fundamental postulate of both is that similar particles are indistinguishable, but in one case symmetric solutions only, and in the other case antisymmetric solutions only, are permitted.

50b. Probability of Eigenstates.—Before proceeding to develop the consequences of the quantum statistics, it is necessary to introduce the postulatory basis of these statistics, equivalent to the postulate of equal a priori probability of extensions of equal volume in γ -space. Every solution of the wave equation for any system is an eigenfunction for that system, and each one of these eigenfunctions, representing a different probability density, is called an *eigenstate* of the system (cf. Section 6a). It may now be postulated that every eigenstate has an equal a priori probability; the eigenstate of wave mechanics is thus the equivalent of the unit cell in the γ -space of classical statistical mechanics. There is, of course, no direct proof of this postulate, although it certainly appears to be a reasonable one from general considerations.

It will be seen later that for a system involving n distinguishable molecules, or other particles, for which there are no restrictions concerning the symmetry of the eigenfunctions, the assumption of the equal probabilities of eigenstates leads to the same results as does that concerning equal volumes in γ -space. The two postulates may, therefore, be regarded as equivalent, one being stated in the language of classical mechanics while the other uses the concepts of the wave mechanics.

50c. Equilibrium in Quantum Statistics.—The Liouville theorem and the microcanonical ensemble of classical statistical mechanics have their equivalents in quantum mechanics; the essential difference is that the density in phase space is replaced by a *density matrix*, which may be regarded as its wave mechanical equivalent. In the language of the quantum mechanics, the microcanonical ensemble is one in which the density matrix has a definite value, independent of time, when the eigenvalue of the energy lies between the limits of E and $E + \delta E$, and is zero outside this range. The total energy of the system cannot be regarded as precisely constant, for there is an uncertainty ΔE , which is related to the time Δt available for observation, by

the Heisenberg principle in the form

$$\Delta E \Delta t \approx h.$$

The magnitude of the range δE stipulated in defining the microcanonical ensemble must be small enough so that it may be treated as an infinitesimal quantity, but must, at the same time, be large in comparison with the uncertainty ΔE . In this ensemble there are equal probabilities of all the different eigenstates corresponding to any eigenvalue of the energy lying in the specified range. A microcanonical ensemble defined in this manner, like the corresponding classical ensemble, will be in statistical equilibrium, and from the observational point of view may be regarded as representing the steady state of the system.

There are certain other respects in which the classical treatment requires modification. In this treatment it was assumed that a continuous variation in the energy is possible, but the quantum theory permits a molecule to have only certain definite energy values. In some instances, each energy level represents a single eigenstate and will have one eigenfunction; however, as a result of various circumstances, a particular level may be degenerate (cf. Section 6a), that is, there may be several eigenfunctions associated with the same, or approximately the same, eigenvalue of the energy. The number of eigenstates, for the particular energy state, is then equal to the degeneracy of that state. If the degeneracy corresponding to the energy ϵ_i is equal to g_i , then the number of eigenstates for that energy is also g_i . For a non-degenerate state, the number of eigenstates is, of course, unity. Since it has been postulated that every eigenstate has an equal probability, the degeneracy g_i is frequently referred to as the *a priori probability* or *statistical weight* of the particular energy level.

50d. Statistical Considerations.—Consider a system involving a large number n of similar "elements"; the word "element" is used here in a very general sense so as to include all types of particles, such as electrons, protons, neutrons, atoms, molecules, and even photons and vibrational modes. Suppose the coordinates of the similar elements are represented by q_1, q_2, \dots, q_n , and that there are available a total number g of eigenfunctions u , such that $u_a(q_1), u_b(q_2), \dots, u_g(q_n)$ are the solutions of the wave equation for the n individual elements. The complete eigenfunction ψ for the whole system, assuming weak interaction, may then be taken as equal to the product of the eigenfunctions for the separated elements (cf. Section 24a); hence, neglecting the normalizing factor,

$$\psi = u_a(q_1)u_b(q_2) \cdots u_g(q_n). \quad (50.1)$$

If there are no symmetry restrictions, and the elements 1, 2, \dots , n are all distinguishable, this particular solution represents one eigenstate of the system. Any change in the distribution of the n elements among the g elementary wave functions would, on this basis, lead to a new value for ψ , and hence to another possible eigenstate corresponding to the same energy

value. It will be seen subsequently that an eigenfunction of the type represented by equation (50.1) leads to results identical with those derived from classical considerations; it may consequently be regarded, in a limited sense, as the quantum basis of the Maxwell-Boltzmann statistics.

It has been already shown, however, that from the point of view of modern physics, two similar particles cannot be regarded as distinguishable; hence, any change in the assignment of the n elements among the g wave functions does not produce a new eigenstate. The complete eigenfunction ψ for the system is no longer given by equation (50.1), but the proper solution must be a linear combination of the functions resulting from all possible permutations of the n elements among the g elementary wave functions; thus, apart from the normalizing factor

$$\psi = \sum \mathbf{P} u_a(q_1) u_b(q_2) \cdots u_o(q_n), \quad (50.2)$$

where \mathbf{P} stands for the permutation operator. Since the elements are indistinguishable, all the permutations are equivalent and they appear with the same coefficient, taken as unity in equation (50.2).

It is now necessary to consider the effect of symmetry restrictions. The symmetry property is an invariant characteristic of the elements constituting the particular system. It can be shown, both theoretically and experimentally, that the symmetry character is a fundamental property that does not change with time. Suppose, in the first place, that the eigenfunction ψ is to be *symmetric*; an interchange of the coordinates of any two elements, e.g., from $u_a(q_1) u_b(q_2) \cdots u_o(q_n)$ to $u_a(q_2) u_b(q_1) \cdots u_o(q_n)$, should produce no change of sign. This condition is actually satisfied by equation (50.2), which consequently represents the symmetric solution of the wave equation of n indistinguishable elements. It will be seen below that for antisymmetric eigenfunctions it is not possible for the wave functions of any two elements to be the same; this restriction, however, does not apply to the symmetric solution. In the case being considered at present, two or more elements may be associated with any particular elementary wave function; thus $u_a(q_i)$ and $u_b(q_i)$ may be the same. The postulate of a system of indistinguishable elements for which symmetric solutions are alone possible is the foundation of the *Bose-Einstein statistics*. This type of quantum statistics is found to be applicable to photons, and also to the nuclei of atoms containing an even number of fundamental particles, i.e., of protons and neutrons. In general, any atom or molecule containing an even number of electrons, of protons and of neutrons satisfies the Bose-Einstein statistics.

If, as before, the n particles are indistinguishable, but the solution of the wave equation is *antisymmetric* in character, it is necessary to modify equation (50.2) by introducing the symbol \pm before the summation sign; thus,

$$\psi = \sum \pm \mathbf{P} u_a(q_1) u_b(q_2) \cdots u_o(q_n), \quad (50.3)$$

the sign being positive or negative according as the number of permutations is even or odd (cf. Section 24a). In these circumstances no two particles

can have the same elementary wave function, as may be seen in the following manner. Suppose the wave functions u_a and u_b , associated with the indistinguishable elements 1 and 2, are identical; then for every permutation contained in the summation of equation (50.3), there will be one of *equal value but of opposite sign* resulting from the exchange of the elements 1 and 2. The whole sum, giving the complete eigenfunction of the system, would consequently be zero. Since this is impossible, it is evident that for an antisymmetric solution of the wave equation, no two particles can be associated with the same elementary eigenfunction. The *Fermi-Dirac statistics*, which applies to all fundamental material particles, viz., electrons, protons and neutrons, and to nuclei containing an odd number of such particles, is based on the supposition of indistinguishable elements which can exist in antisymmetric states only.

50e. The Bose-Einstein Statistics.—Suppose the n indistinguishable elements that constitute the system under consideration are divided into a series of quantum groups or levels, with the numbers of elements, $n_1, n_2, \dots, n_i, \dots$; in each group the energy is (almost) constant, viz., $\epsilon_1, \epsilon_2, \dots, \epsilon_i, \dots$, respectively. Then since the total number of elements is constant, and the total energy of the system is also constant, within narrow limits, it follows that

$$\sum_i n_i = n = \text{constant}, \quad (50.4)$$

and

$$\sum_i \epsilon_i n_i = E = \text{constant}. \quad (50.5)$$

If the degeneracy, i.e., statistical weight, of the i th level, in general, is equal to g_i , the total number of eigenstates for the group of n_i elements is equal to the number of ways in which the n_i elements can be distributed among the g_i wave functions. Since the complete eigenfunction for the Bose-Einstein statistics is to be symmetric, there is no restriction as to the number of elements associated with each particular function. The required number of different ways is equivalent to that in which n_i indistinguishable particles can be distributed in a box divided into g_i compartments, without any restriction as to the number in each of the compartments. Imagine a box divided by $g_i - 1$ partitions into g_i sections; the n_i particles are then supposed to be distributed among these sections. The total number of permutations of the n_i particles and the $g_i - 1$ partitions is $(n_i + g_i - 1)!$. Since the n_i particles are indistinguishable, permutations among the particles themselves do not really produce a new arrangement. The total number just given should therefore be divided by $n_i!$. Further, the permutations among the $g_i - 1$ partitions do not alter the fact that there are still g_i sections; hence, division of the total number of permutations by $(g_i - 1)!$ is also necessary. The number of ways,

$$\frac{(n_i + g_i - 1)!}{n_i! (g_i - 1)!},$$

of distributing the n_i particles among the g_i compartments, is then equal to the number of different eigenstates in any group containing n_i elements.

The total number n of elements is divided into a set of groups containing $n_1, n_2, \dots, n_i, \dots$, respectively, but since the elements are indistinguishable, there is only one way in which this subdivision can be made. In each group the number of eigenstates is given by an expression of the same type as that just derived for the i th group, and hence the total number G of eigenstates for the whole system, corresponding to the specified distribution of the n elements, is given by

$$G = \frac{(n_1 + g_1 - 1)!}{n_1!(g_1 - 1)!} \cdot \frac{(n_2 + g_2 - 1)!}{n_2!(g_2 - 1)!} \cdots \frac{(n_i + g_i - 1)!}{n_i!(g_i - 1)!} \cdots \quad (50.6)$$

$$= \prod_i \frac{(n_i + g_i - 1)!}{n_i!(g_i - 1)!} \quad (50.7)$$

where the symbol \prod is used to indicate the product of a series of similar terms. Introducing now the postulate of the equal a priori probability of eigenstates, it follows that the probability W of the system having the particular distribution specified, is proportional to the total number of eigenstates; hence,

$$W = \prod_i \frac{(n_i + g_i - 1)!}{n_i!(g_i - 1)!} \times \text{constant}, \quad (50.8)$$

for the Bose-Einstein statistics.

The procedure is now similar to that employed in Section 48a for the derivation of the classical Maxwell-Boltzmann equation; the condition of maximum probability of the system is found by setting $\delta \ln W$ equal to zero. Upon taking logarithms of equation (50.8), this becomes

$$\ln W = \sum_i \{ \ln (n_i + g_i - 1)! - \ln n_i! - \ln (g_i - 1)! \} + \text{constant}, \quad (50.9)$$

and making use of the Stirling formula

$$\ln n! = n \ln n - n,$$

which is applicable provided all the n_i 's and the g_i 's are very large numbers, it is found that

$$\ln W = \sum_i \{ (n_i + g_i) \ln (n_i + g_i) - n_i \ln n_i - g_i \ln g_i \} + \text{constant}, \quad (50.10)$$

where $n_i + g_i - 1$ and $g_i - 1$ have been taken as equal to $n_i + g_i$ and g_i , respectively. Since the number n_i is supposed to be very large, it may be treated as a continuous variable, and hence differentiation of equation (50.10) with respect to n_i gives for the most probable state of the system

$$\delta \ln W = \sum_i \{ \ln n_i - \ln (n_i + g_i) \} \delta n_i = 0$$

or

$$\sum_i \left(\ln \frac{n_i}{n_i + g_i} \right) \delta n_i = 0. \quad (50.11)$$

As before, the restrictions of constant number of elements n and of constant total energy for the whole system, as given by equations (50.4) and (50.5), may now be introduced. Since n_i and g_i , for each quantum group, have been assumed to be large, the distribution of energy within a group may be regarded as virtually continuous, at least over a narrow range; it is thus possible to write

$$\delta n = \sum \delta n_i = 0$$

and

$$\delta E = \sum \epsilon_i \delta n_i = 0.$$

Applying the Lagrange method of undetermined multipliers to these relationships in combination with equation (50.11), the result is

$$\sum_i \left(\ln \frac{n_i}{n_i + g_i} + \alpha + \beta \epsilon_i \right) \delta n_i = 0. \quad (50.12)$$

Since the variations δn_i are independent of one another,

$$\ln \frac{n_i}{n_i + g_i} + \alpha + \beta \epsilon_i = 0, \quad (50.13)$$

and hence,

$$\begin{aligned} \ln \left(\frac{g_i}{n_i} + 1 \right) &= \alpha + \beta \epsilon_i \\ \therefore \frac{g_i}{n_i} + 1 &= e^{\alpha + \beta \epsilon_i} \end{aligned} \quad (50.14)$$

or

$$n_i = \frac{g_i}{e^{\alpha + \beta \epsilon_i} - 1}. \quad (50.15)$$

The final equation (50.15) is the mathematical representation of the Bose-Einstein statistics for the most probable distribution of elements among energy levels.

50f. The Fermi-Dirac Statistics.—In deriving the consequences of the Fermi-Dirac statistics, which postulates that the n similar elements constituting a given system are indistinguishable, and that only antisymmetric solutions of the wave equation are permitted, it is assumed, as in the previous case, that the number of elements is constant and so also is the total energy. In the determination of the total number of eigenstates for the system of n_i elements in the i th group, where g_i eigenfunctions are available to each element, it must be remembered that because of the restriction of the Fermi-Dirac statistics to antisymmetric states, only one of the n_i elements can be associated with each of the g_i elementary wave functions. It follows, of

course, that g_i must be greater than or equal to n_i , since there must be at least one elementary wave function for every element in the group. The required number of eigenstates is equivalent to the number of combinations of g_i articles taken n_i at a time; this gives

$$\frac{g_i!}{n_i!(g_i - n_i)!}$$

for the number of different eigenstates in the i th group. The total number of eigenstates G for the whole system is then

$$G = \frac{g_1!}{n_1!(g_1 - n_1)!} \cdot \frac{g_2!}{n_2!(g_2 - n_2)!} \cdots \frac{g_i!}{n_i!(g_i - n_i)!} \cdots \quad (50.16)$$

$$= \prod_i \frac{g_i!}{n_i!(g_i - n_i)!}, \quad (50.17)$$

and the probability of the given state is

$$W = \prod_i \frac{g_i!}{n_i!(g_i - n_i)!} \times \text{constant}. \quad (50.18)$$

Proceeding as in the previous case, it is seen that

$$\ln W = \sum_i \{\ln g_i! - \ln n_i! - \ln (g_i - n_i)!\} + \text{constant},$$

and introduction of the Stirling approximation, assuming that $g_i - n_i$ is very large, as well as n_i and g_i , gives

$$\ln W = \sum_i \{(n_i - g_i) \ln (g_i - n_i) - n_i \ln n_i + g_i \ln g_i\} + \text{constant}. \quad (50.19)$$

The condition for the most probable state is then

$$\delta \ln W = \sum_i \{\ln n_i - \ln (g_i - n_i)\} \delta n_i = 0,$$

$$\therefore \sum_i \left(\ln \frac{n_i}{g_i - n_i} \right) \delta n_i = 0. \quad (50.20)$$

Upon introducing the conditions of constant number of elements in the system and constant total energy, and using the method of undetermined multipliers, it is found that

$$\sum_i \left(\ln \frac{n_i}{g_i - n_i} + \alpha + \beta \epsilon_i \right) \delta n_i = 0,$$

and since the δn_i 's are arbitrary, it follows that

$$\ln \frac{n_i}{g_i - n_i} + \alpha + \beta \epsilon_i = 0, \quad (50.21)$$

$$\therefore \ln \left(\frac{g_i}{n_i} - 1 \right) = \alpha + \beta \epsilon_i,$$

and

$$\frac{g_i}{n_i} - 1 = e^{\alpha + \beta \epsilon_i}, \quad (50.22)$$

or

$$n_i = \frac{g_i}{e^{\alpha + \beta \epsilon_i} + 1}. \quad (50.23)$$

The most probable distribution, among the various energy levels, of the elements of a system obeying the Fermi-Dirac statistics is given by equation (50.23).

50g. The Maxwell-Boltzmann Statistics.—If the eigenfunction represented by equation (50.1) is a satisfactory solution of the wave equation for a system of n identical elements, it means that the elements are distinguishable, and that there are no symmetry restrictions that must be applied. In order to calculate the total number of eigenstates for a system that satisfies these requirements, it is convenient to consider first the number of ways of distributing the n distinguishable elements among the various possible groups; the result is

$$\frac{n!}{n_1! n_2! \dots n_i! \dots}$$

In each group the n_i elements may be distributed among g_i elementary wave functions. Since symmetry considerations do not arise, there is no restriction as to the number of elements associated with each wave function, and so the total number of ways in which the distribution may be made is equal to $g_i^{n_i}$ in each group. The complete number of eigenstates for the system as a whole is therefore given by

$$G = n! \frac{g_1^{n_1}}{n_1!} \cdot \frac{g_2^{n_2}}{n_2!} \dots \frac{g_i^{n_i}}{n_i!} \dots \quad (50.24)$$

$$= n! \prod_i \frac{g_i^{n_i}}{n_i!}, \quad (50.25)$$

and the corresponding probability is

$$W = n! \prod_i \frac{g_i^{n_i}}{n_i!} \times \text{constant}. \quad (50.26)$$

Taking logarithms, and then applying the Stirling approximation, assuming

n_i to be very large, it is found that

$$\ln W = n \ln n + \sum_i (n_i \ln g_i - n_i \ln n_i) + \text{constant.} \quad (50.27)$$

As before, the condition for the most probable state is obtained from

$$\delta \ln W = \sum_i \left(\ln \frac{n_i}{g_i} + 1 \right) \delta n_i = 0, \quad (50.28)$$

and application of the same procedure as in previous cases leads to the result

$$\ln \frac{n_i}{g_i} + \alpha + \beta \epsilon_i = 0, \quad (50.29)$$

or,

$$\begin{aligned} \ln \frac{g_i}{n_i} &= \alpha + \beta \epsilon_i, \\ \therefore \frac{g_i}{n_i} &= e^{\alpha + \beta \epsilon_i}, \end{aligned} \quad (50.30)$$

and hence

$$n_i = \frac{g_i}{e^{\alpha + \beta \epsilon_i}}. \quad (50.31)$$

If this result is compared with equation (48.13) it will be seen that, apart from the statistical weight factor, which does not appear in the simple classical treatment, equation (50.31) is identical with the Maxwell-Boltzmann distribution law.

50h. Comparison of the Three Statistics.—For purposes of comparison of the three forms of statistics, the essential equations obtained in each case will be repeated here; they are:

(i) Bose-Einstein Statistics.

$$\frac{g_i}{n_i} + 1 = e^{\alpha + \beta \epsilon_i} \quad \text{or} \quad n_i = \frac{g_i}{e^{\alpha + \beta \epsilon_i} - 1}.$$

(ii) Fermi-Dirac Statistics.

$$\frac{g_i}{n_i} - 1 = e^{\alpha + \beta \epsilon_i} \quad \text{or} \quad n_i = \frac{g_i}{e^{\alpha + \beta \epsilon_i} + 1}.$$

(iii) Maxwell-Boltzmann Statistics.

$$\frac{g_i}{n_i} = e^{\alpha + \beta \epsilon_i} \quad \text{or} \quad n_i = \frac{g_i}{e^{\alpha + \beta \epsilon_i}}.$$

It is evident that although the distribution laws derived from the three kinds of statistics are different, there will be certain conditions under which Bose-Einstein and Fermi-Dirac statistics yield results virtually identical with those given by the Maxwell-Boltzmann statistics. This will occur if

g_i/n_i is very large in comparison with unity, so that

$$\frac{g_i}{n_i} + 1 \approx \frac{g_i}{n_i} - 1 \approx \frac{g_i}{n_i}.$$

In these circumstances, all three expressions for the distribution law will become equivalent to that for the Maxwell-Boltzmann statistics. In general, provided the temperature is not too low or the pressure too high, the number of available eigenstates g_i is large in comparison with the number of elements n_i , so that g_i/n_i is then much greater than unity. It follows, therefore, that for almost all conditions under which normal gases exist, the classical distribution law should be adequate to describe their actual behavior, within the possible limits of experimental observation. There are a limited number of cases in which the classical distribution law is not applicable, but these are very few; they are chiefly three, viz., radiation, liquid helium II, and the "electron gas" in metals, apart from conditions of extremely low temperatures or high pressures.

50i. Evaluation of the Constant β .—For a system obeying the Maxwell-Boltzmann statistics, it is obvious that the value of β in equation (50.31) must be identical with the β in equation (48.13), for it is possible to carry through the same treatment for calculating the total energy, and thus to arrive at the result $\beta = 1/kT$. The values of β in equations (50.15) and (50.23), for the Bose-Einstein and Fermi-Dirac statistics, respectively, cannot be derived in this manner, but it is not difficult to show that they must both also be equal to $1/kT$. In the first place, it is evident that if the Bose-Einstein or Fermi-Dirac systems are studied at such temperatures and pressures that g_i/n_i is large, their behavior is almost classical. The value of β under these conditions must then be equal to $1/kT$. Since β is a constant which does not change with the conditions, it should have the same value, viz., $1/kT$, in the distribution laws derived from the three types of statistics.

The same conclusion may be reached by imagining a system containing a large number of elements of different kinds, some behaving in a classical manner, others obeying one form of quantum statistics, while still others obey the alternative form. The system may be supposed to be in a condition of statistical and temperature equilibrium. The total number of elements in the system is constant, and so also is the number of each kind; the energy is also assumed to be constant within narrow limits. Remembering that the total probability of the system is equal to the product of the probabilities for the various kinds of elements, it can be shown by the method of Section 48c that the constant β must be the same for all the elements irrespective of their symmetry or other characteristics. It is then possible to represent the three distribution laws by means of the general equation

$$n_i = \frac{g_i}{Be^{1/kT} + c}, \quad (50.32)$$

where c is equal to -1 for the Bose-Einstein, to $+1$ for the Fermi-Dirac, and to zero for the classical statistics; the constant B , equal to e^{α} , varies with the nature of the elements constituting the system.

50j. Correction of Number of Eigenstates in Classical Statistics.—Although the three forms of statistics lead to the same distribution law under reasonable conditions, there is one important respect in which they differ; this is ascribable to the fact that the Maxwell-Boltzmann statistics is based on the assumption that the n identical elements constituting the system are distinguishable, whereas according to the quantum statistics this is not the case. The consequence of this difference may be readily seen by considering the situation in which the n elements are all in different groups, that is, when all the n_i values are unity. In these circumstances all the g_i 's will be greater than the respective n_i 's, and the conditions should be such that all three statistics should lead to the same result. It can be readily seen from equations (50.7) and (50.17) that the total number of eigenstates, for both the Bose-Einstein and Fermi-Dirac statistics, will be equal to $\prod g_i$, i.e., to the product of all the g_i terms. However, from equation (50.25) it is found that for the same distribution the Maxwell-Boltzmann statistics leads to the expectation of $n! \prod g_i$ eigenstates. The $n!$ fold greater number calculated for these statistics arises because the n elements are assumed to be distinguishable. It follows, therefore, that if the results of the classical statistics are to agree with those of the quantum statistics, under such conditions that the g_i 's are greater than the n_i 's, it is necessary that the equation (50.25) for the number of eigenstates be divided by $n!$. Since $n!$ is a constant, it can be readily seen that the change in the value of G does not affect the final distribution equation (50.31). The importance of introducing the $n!$ correction will become apparent, however, in the discussion of the contribution to entropy made by the translational energy (Section 58e).

It is of interest to record that the division of the number of unit cells (complexions) in phase space—the equivalent of the number of eigenstates—by $n!$ was introduced arbitrarily into classical mechanics in order to make an obviously needed correction. Nevertheless, the real explanation for the necessity of applying this correction was not evident until the advent of the new quantum mechanics.

51a. Relation Between Eigenstates and Phase Volume.—It is a well known fact, expressed in the form of Bohr's correspondence principle, that in the limit, when the quantum numbers are large, at least relative to the energy, quantum and classical treatments lead to identical results. An illustration of this correspondence is, in fact, to be found in the equivalence of the distribution laws derived from the classical and quantum statistics at reasonably high temperatures and not too large pressures. In order to extend the correlation between the different forms of statistics, it is of interest to consider the relationship between the number of unit cells, i.e., the volume, of phase space occupied by a system, and the number of eigenstates available to that system. According to the postulates made in the present chapter,

these numbers are proportional to the probability of the system, in the classical and quantum treatments, respectively, and some connection between them, in the correspondence principle limit, is to be expected.

Although the word "volume" has been used to refer to the extension in phase space, it is evident that the quantity under consideration does not have the dimensions of volume in the usual sense of this term. The product of p and q has the dimensions of *action*, i.e., ML^2/T , and hence for a system having f degrees of freedom, the dimensions of the "volume" in phase space will be $(ML^2/T)^f$. The Planck constant h has the dimensions ML^2/T , and hence it seems reasonable to identify the classical volume of a unit cell in γ -space with the quantity h^f ; thus,

$$\delta q_1 \cdots \delta q_f \delta p_1 \cdots \delta p_f = h^f, \quad (51.1)$$

may be expected to be a satisfactory correlation at the correspondence principle limit. This equivalence between the volume in phase space and the number of eigenstates for a system may then be represented by

$$\frac{1}{h^f} \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} dq_1 \cdots dp_f = g. \quad (51.2)$$

Justification for the foregoing suggestion is provided by a number of considerations. In the first place, there is the outstanding fact that it leads to satisfactory results, as will be evident shortly. Secondly, in the older quantum theory, the integral of $p dq$ over the whole path between two successive energy states was taken as equal to h . Finally, the proposed correlation is in harmony with the newer quantum theory. According to the Heisenberg uncertainty principle, the coordinate q and conjugate momentum p of a system can be stated only with an accuracy lying within the limits of Δq and Δp , respectively; these uncertainties are related by the expression $\Delta q \Delta p \approx h$ (cf. Section 3b). The uncertainty product $\Delta q \Delta p$ is equivalent to the volume in the γ -space occupied by a system having one degree of freedom, and this should be equal to the Planck constant h . In general, for a system of f degrees of freedom, the uncertainty product representing the uncertainty of defining the position of the system in phase space, will be equal to h^f . It follows, therefore, that every extension h^f in γ -space will be equivalent to a single state (eigenstate) of the system. The total volume of the system in the γ -space, as determined classically, divided by h^f should thus be equal to the number of eigenstates of the system, in agreement with equation (51.2).

51b. Number of Eigenstates in an Energy Range.—It was found in Section 7, using the methods of wave mechanics, that the translational energy ϵ of a point particle, possessing three degrees of freedom, moving in a potential-free rectangular box with edges of length a , b and c , respectively,

could be represented by the equation

$$\epsilon = \frac{h^2}{8m} \left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right), \quad (51.3)$$

where n_x , n_y and n_z are zero or integral quantum numbers for motion of the particle parallel to the three cartesian axes x , y and z . In order to simplify the treatment, without affecting the nature of the results obtained, it will be assumed that the containing vessel is a cube of side l , so the a , b and c may each be replaced by l ; equation (51.3) then becomes

$$\epsilon = \frac{h^2}{8ml^2} (n_x^2 + n_y^2 + n_z^2). \quad (51.4)$$

For the present purpose, it is desired, in the first place, to calculate the total number of eigenstates for energies lying between zero and the value ϵ . To do this, it is convenient to consider first the energy in one, then in two, and finally in three degrees of freedom. For one degree of freedom, e.g., parallel to the x axis, the energy is

$$\epsilon_1 = \frac{h^2}{8ml^2} n_x^2, \quad (51.5)$$

and the number g_1 of quantum states with energies lying between zero and ϵ_1 is evidently equal to n_x ; hence from equation (51.5)

$$g_1 = n_x = \frac{2l}{h} (2m\epsilon_1)^{1/2}. \quad (51.6)$$

If the energy is in two degrees of freedom, e.g., x and y , the energy ϵ_2 is then given by

$$\epsilon_2 = \frac{h^2}{8ml^2} (n_x^2 + n_y^2) \quad (51.7)$$

$$= \frac{h^2}{8ml^2} r^2, \quad (51.8)$$

where

$$r^2 = n_x^2 + n_y^2. \quad (51.9)$$

The number of eigenstates with energy lying between zero and ϵ_2 in two degrees of freedom can be derived in a convenient manner by considering a system of two cartesian coordinates, and plotting the values of n_x and n_y , respectively, in the two directions (Fig. 39). For each positive integral or zero value of n_x and n_y there will be a point on the diagram, representing a definite quantum state (eigenstate) in the two degrees of freedom. If the energy of the system is not to exceed ϵ_2 , as given by equation (51.7), then it follows from equation (51.9) that the values of n_x and n_y must be such that

$$n_x^2 + n_y^2 \leq r^2, \quad (51.10)$$

and every point in Fig. 39 satisfying this requirement represents a possible eigenstate for energy between zero and ϵ_2 , in two degrees of freedom. The total number of such points is obtained by drawing the quadrant of a circle of radius r , having its center at the origin of Fig. 39; all the points lying

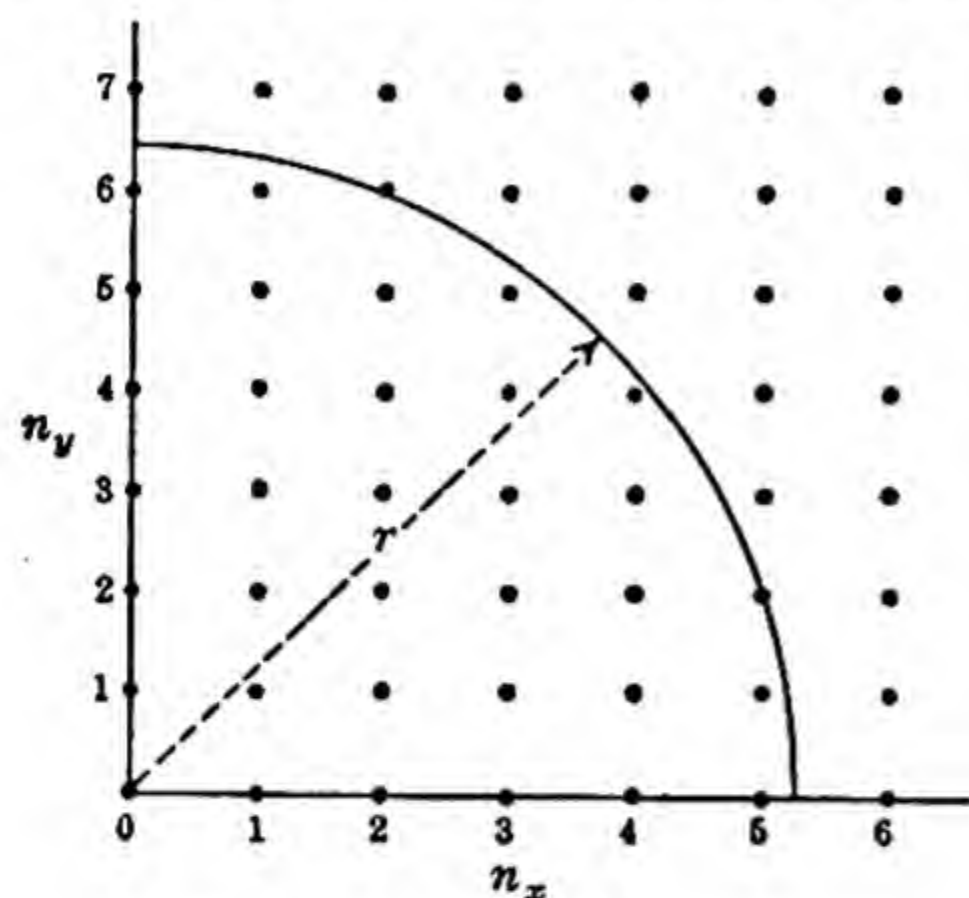


FIG. 39. Eigenstates of energy in two degrees of freedom

within the quadrant satisfy equation (51.10), and hence the required number of eigenstates is equal to this number of points. For a sufficiently large value of the energy, so that the corresponding quantum numbers n_x and n_y are large, it is evident that each unit area in Fig. 39 will contain, on the average, one point. The number g_2 of eigenstates under consideration is thus equal to the area of the quadrant of the circle of radius r ; hence,

$$\begin{aligned} g_2 &= \frac{1}{4}\pi r^2 \\ &= \frac{\pi l^2}{h^2} 2m\epsilon_2. \end{aligned} \quad (51.11)$$

Extending the arguments to three degrees of freedom, the total translational energy ϵ is given by equation (51.4) as

$$\epsilon = \frac{h^2}{8ml^2} r^2, \quad (51.12)$$

where r^2 is now defined by

$$r^2 = n_x^2 + n_y^2 + n_z^2, \quad (51.13)$$

and all eigenstates with energy lying between zero and ϵ must satisfy the condition

$$n_x^2 + n_y^2 + n_z^2 \leq r^2.$$

The required number of states can be evaluated by making a three-dimensional plot of n_x , n_y and n_z , and counting the number of points, for which these quantum numbers are integral, lying within the octant of a sphere of radius r . For sufficiently large values of the energy, each point will correspond to one unit cube in this octant, and hence its volume gives the required number of eigenstates. The result is consequently

$$\begin{aligned} g &= \frac{1}{8}(\frac{4}{3}\pi r^3) \\ &= \frac{4\pi l^3}{3h^3} (2m\epsilon)^{3/2} \end{aligned} \quad (51.14)$$

$$= \frac{4\pi V}{3h^3} (2m\epsilon)^{3/2}, \quad (51.15)$$

where V , equal to l^3 , is the volume of the box containing the particle.

It is desired to know the number of states with eigenvalues of the translational energy lying between ϵ and $\epsilon + \Delta\epsilon$, where $\Delta\epsilon$ is small but large enough to contain an appreciable number of energy levels. Under these conditions, the number of eigenstates $g(\Delta\epsilon)$ is obtained by differentiation of equation (51.15); thus,

$$g(\Delta\epsilon) = \frac{4\pi m V}{h^3} (2m\epsilon)^{1/2} \Delta\epsilon. \quad (51.16)$$

It is of interest to show that this same result can be obtained by utilizing the postulate that the volume of a unit cell in classical phase (γ) space can be taken as equal to h^f . For a point particle, such as that under consideration, there are three degrees of freedom; the three coordinates may be represented by x , y and z , and the corresponding momenta, viz., p_x , p_y and p_z , are $m\dot{x}$, $m\dot{y}$ and $m\dot{z}$. The number of eigenstates according to equation (51.2) is then given by

$$\begin{aligned} g &= \frac{1}{h^3} \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} dx dy dz dp_x dp_y dp_z \\ &= \frac{m^3}{h^3} \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} d\dot{x} d\dot{y} d\dot{z}. \end{aligned} \quad (51.17)$$

Integration over the three coordinates x , y , z , gives the volume V of the containing vessel, and hence

$$g = \frac{m^3 V}{h^3} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} d\dot{x} d\dot{y} d\dot{z}. \quad (51.18)$$

Changing to polar coordinates (cf. Section 49a), it is found that

$$g(dc) = \frac{m^3 V}{h^3} \int_0^\pi \int_0^{2\pi} \int_c^{c+dc} c^2 \sin \theta d\theta d\phi dc \quad (51.19)$$

$$= \frac{4\pi m^3 V}{h^3} c^2 dc, \quad (51.20)$$

where, as before, c^2 is equal to $\dot{x}^2 + \dot{y}^2 + \dot{z}^2$. It will be noted that the integration limits for θ are zero and π , for ϕ they are zero and 2π , while for c the limits are c and $c + dc$; the result is the number of eigenstates for the particle with speeds lying between c and $c + dc$, irrespective of direction. Changing the variable by means of the relationship derived in Section 49a, viz.,

$$c^2 dc = \frac{(2\epsilon)^{1/2}}{m^{3/2}} d\epsilon,$$

where ϵ is the translational energy, it follows that equation (51.20) may be

written as

$$g(d\epsilon) = \frac{4\pi mV}{h^3} (2m\epsilon)^{1/2} d\epsilon \quad (51.21)$$

for the number of eigenstates with energy lying in the range ϵ to $\epsilon + d\epsilon$. This result is in agreement with that expressed by equation (51.16), the only difference being that in the latter case quantum considerations require the energy range $\Delta\epsilon$ to be appreciable in magnitude.

51c. Eigenstates and the Maxwell-Boltzmann Equation.—The distribution law equation (50.31) for the Maxwell-Boltzmann statistics, which may be written as

$$n_i = \frac{g_i}{B e^{\epsilon_i/kT}}, \quad (51.22)$$

where B is equal to e^a , can also be put into the form

$$dn = \frac{g(d\epsilon)}{B e^{\epsilon/kT}} \quad (51.23)$$

for the number dn of particles whose energy lies between ϵ and $\epsilon + d\epsilon$; as before, $g(d\epsilon)$ is the number of eigenstates for this energy range. If the energy is translational in character, it is possible to utilize equation (51.21) for $g(d\epsilon)$; an additional statistical weight factor Q_i must be introduced to allow for other forms of degeneracy, such as those due to spin, and then equation (51.23) becomes

$$dn = \frac{Q_i}{B} \cdot \frac{4\pi mV}{h^3} (2m\epsilon)^{1/2} e^{-\epsilon/kT} d\epsilon. \quad (51.24)$$

In order to evaluate the constant B , equation (51.24) must be integrated; for this purpose it is convenient to define the variable x , thus

$$x = \frac{\epsilon}{kT},$$

so that equation (51.24) can be written as

$$dn = \frac{Q_i}{B} \cdot \frac{2V}{\pi^{1/2}} \cdot \frac{(2\pi mkT)^{3/2}}{h^3} x^{1/2} e^{-x} dx. \quad (51.25)$$

Integration of this expression then leads to

$$\begin{aligned} \int_0^n dn &= n = \frac{Q_i}{B} \cdot \frac{2V}{\pi^{1/2}} \cdot \frac{(2\pi mkT)^{3/2}}{h^3} \int_0^\infty x^{1/2} e^{-x} dx \\ &= \frac{Q_i}{B} \cdot \frac{(2\pi mkT)^{3/2} V}{h^3}, \\ \therefore B &= \frac{Q_i}{n} \cdot \frac{(2\pi mkT)^{3/2} V}{h^3}. \end{aligned} \quad (51.26)$$

Introduction of this value of B into equation (51.24), gives

$$dn = \frac{2\pi n}{(\pi kT)^{3/2}} e^{-\epsilon/kT} \epsilon^{1/2} d\epsilon, \quad (51.27)$$

which is identical with equation (49.10), the Maxwell equation for the distribution of the translational energy of molecules.

The total energy E of the n molecules can be represented by

$$E = \int_0^\infty \epsilon dn,$$

and upon utilization of the equation (51.27) for dn , it follows that

$$\begin{aligned} E &= \frac{2\pi n}{(\pi kT)^{3/2}} \int_0^\infty \epsilon^{3/2} e^{-\epsilon/kT} d\epsilon \\ &= \frac{3}{2} n kT. \end{aligned} \quad (51.28)$$

For a mole of gas, n is equal to the Avogadro number, and equation (51.28) then gives the expected value $\frac{3}{2}RT$ for the translational energy of an ideal gas.

APPLICATIONS OF BOSE-EINSTEIN STATISTICS

52a. Bose-Einstein Systems.—It is now possible to consider the changes that are introduced into the calculations for systems obeying the Bose-Einstein statistics. The system is supposed to consist of weakly interacting point particles, so that the energy, as in the preceding section, may be regarded as entirely translational in character; the results will therefore be particularly applicable to a monatomic gas. For the present purpose, the Bose-Einstein equation may be written in a form analogous to equation (51.23), viz.,

$$dn = \frac{g(d\epsilon)}{Be^{\epsilon/kT} - 1}, \quad (52.1)$$

where dn and $g(d\epsilon)$ have the same significance as above; B is again equivalent to e^α . Introducing the value of $g(d\epsilon)$ for translational energy as given by equation (51.21), and including an additional statistical weight factor Q_i to allow for other forms of degeneracy, equation (52.1) becomes

$$dn = \frac{4\pi mV}{h^3} Q_i (2m\epsilon)^{1/2} \frac{d\epsilon}{Be^{\epsilon/kT} - 1}. \quad (52.2)$$

Introducing the variable x , as before, equation (52.2) transforms into

$$dn = \frac{2Q_i}{\pi^{1/2}} \cdot \frac{(2\pi mkT)^{3/2} V}{h^3} \cdot \frac{x^{1/2} dx}{Be^x - 1}. \quad (52.3)$$

For reasons which will appear in Chapter VIII, it is convenient to define a

quantity Q_t by the expression

$$Q_t = \frac{(2\pi mkT)^{3/2}}{h^3} V. \quad (52.4)$$

Further, the product of Q_t and the degeneracy factor Q_i may be represented by Q ; thus

$$Q = Q_t Q_i. \quad (52.5)$$

With these modifications, equation (52.3) becomes

$$dn = \frac{2Q}{\pi^{1/2}} \cdot \frac{x^{1/2} dx}{Be^x - 1}, \quad (52.6)$$

and upon integration,

$$n = \frac{2Q}{\pi^{1/2}} \int_0^\infty \frac{x^{1/2} dx}{Be^x - 1}. \quad (52.7)$$

The total translational energy E of the n molecules in the system is then given by

$$E = \int_0^\infty \epsilon dn = \frac{2kTQ}{\pi^{1/2}} \int_0^\infty \frac{x^{3/2} dx}{Be^x - 1}. \quad (52.8)$$

The evaluation of the integrals in equations (52.7) and (52.8) is simplified for the case in which B is greater than unity, i.e., α in equation (50.15) is positive. This condition must be satisfied for a Bose-Einstein system, for otherwise the value of n , in equation (50.15) would become negative at sufficiently low energies; this is, of course, impossible. In these circumstances it is possible to write

$$(Be^x - 1)^{-1} = \frac{e^{-x}}{B} \left(1 + \frac{e^{-x}}{B} + \frac{e^{-2x}}{B^2} + \dots \right)$$

as a rapidly converging power series; then

$$\begin{aligned} \int_0^\infty \frac{x^{1/2} dx}{Be^x - 1} &= \frac{1}{B} \int_0^\infty e^{-x} x^{1/2} dx + \frac{1}{B^2} \int_0^\infty e^{-2x} x^{1/2} dx + \dots \\ &= \frac{\pi^{1/2}}{2B} \left(1 + \frac{1}{2^{3/2}B} + \frac{1}{3^{3/2}B^2} + \dots \right). \end{aligned} \quad (52.9)$$

It follows then from equation (52.7) that

$$n = \frac{Q}{B} \left(1 + \frac{1}{2^{3/2}B} + \frac{1}{3^{3/2}B^2} + \dots \right), \quad (52.10)$$

$$\therefore B = \frac{Q}{n} \left(1 + \frac{1}{2^{3/2}B} + \frac{1}{3^{3/2}B^2} + \dots \right). \quad (52.11)$$

The integral in equation (52.8) can now be evaluated by writing

$$\begin{aligned} \int_0^\infty \frac{x^{3/2} dx}{Be^x - 1} &= \frac{1}{B} \int_0^\infty e^{-x} x^{3/2} dx + \frac{1}{B^2} \int_0^\infty e^{-2x} x^{3/2} dx + \dots \\ &= \frac{3\pi^{1/2}}{4B} \left(1 + \frac{1}{2^{5/2}B} + \frac{1}{3^{5/2}B^2} + \dots \right), \end{aligned} \quad (52.12)$$

and therefore

$$E = \frac{3kTQ}{2B} \left(1 + \frac{1}{2^{5/2}B} + \frac{1}{3^{5/2}B^2} + \dots \right). \quad (52.13)$$

Introducing the value of B given by equation (52.11), the result is

$$E = \frac{3}{2}nkT \left(1 - \frac{1}{2^{5/2}B} - \frac{1}{3^{5/2}B^2} - \dots \right), \quad (52.14)$$

and if, as a first approximation, B is replaced by Q/n , i.e., the classical value given by equation (51.26) to which (52.11) reduces when B is large, equation (52.14) becomes

$$E = \frac{3}{2}nkT \left\{ 1 - \frac{1}{2^{5/2}} \left(\frac{n}{Q} \right) - \frac{1}{3^{5/2}} \left(\frac{n}{Q} \right)^2 - \dots \right\}. \quad (52.15)$$

For 1 mole of gas, n may be replaced by N , the Avogadro number; hence

$$E = \frac{3}{2}RT \left\{ 1 - \frac{1}{2^{5/2}} \left(\frac{N}{Q} \right) - \frac{1}{3^{5/2}} \left(\frac{N}{Q} \right)^2 - \dots \right\}, \quad (52.16)$$

which may be compared with $\frac{3}{2}RT$ for the translational energy of a classical Maxwell-Boltzmann gas.

52b. Gas Degeneration.—The pressure of a Bose-Einstein gas may be derived from the energy by utilizing the relationship $P = 2E/3V$ applicable to a classical ideal gas; however, it is desirable to show that this equation holds also under quantum conditions. This can be done in several ways, but the following simple treatment, although not quite complete, should suffice; it makes use of the familiar thermodynamic equation

$$P = - \left(\frac{\partial E}{\partial V} \right)_s. \quad (52.17)$$

According to equation (51.12), the expression for the energy of a point particle, such as a molecule of an ideal monatomic gas, moving in a cube of side l is

$$\epsilon = \frac{h^2}{8ml^2} r^2,$$

where r^2 is determined by the quantum numbers for the motion. If the

volume of the cube is V , then l^2 is equal to $V^{2/3}$, and hence

$$\epsilon = \frac{h^2}{8mV^{2/3}} r^2. \quad (52.18)$$

It will be seen later (Section 55b) that the entropy of a system depends entirely on the number of eigenstates, and in the case under consideration this number, as given by equation (51.15), is proportional to r^3 . It follows, therefore, that for an energy change at constant entropy the term r^2 in equation (52.18) will remain constant; differentiation of this equation with respect to V then gives

$$\begin{aligned} P &= - \left(\frac{\partial E}{\partial V} \right)_s = \frac{2}{3} \cdot \frac{h^2}{8mV^{5/3}} r^2, \\ &= \frac{2\epsilon}{3V}, \end{aligned}$$

in agreement with the classical relationship. The result derived here is for a single molecule of energy ϵ , but an exactly analogous result, viz.,

$$P = \frac{2E}{3V}, \quad (52.19)$$

would be obtained for a system of n molecules of total translational energy E , occupying the volume V .

Utilizing equation (52.19), in conjunction with equation (52.14), it is seen that

$$P = \frac{nkT}{V} \left(1 - \frac{1}{2^{5/2}B} - \frac{1}{3^{5/2}B^2} - \dots \right). \quad (52.20)$$

For a system containing 1 mole, that is N molecules, in the volume V , this equation becomes

$$P = \frac{RT}{V} \left(1 - \frac{1}{2^{5/2}B} - \frac{1}{3^{5/2}B^2} - \dots \right) \quad (52.21)$$

$$= \frac{RT}{V} \left\{ 1 - \frac{1}{2^{5/2}} \left(\frac{N}{Q} \right) - \frac{1}{3^{5/2}} \left(\frac{N}{Q} \right)^2 - \dots \right\}. \quad (52.22)$$

This result for the pressure of an ideal Bose-Einstein gas is obviously different from that for a classical ideal gas, i.e., RT/V .

It is apparent from equations (52.14) and (52.21) that the deviations from ideal behavior exhibited by a Bose-Einstein gas, generally referred to as *gas degeneration*, depend on the quantity $1/B$. This may be taken as equal to n/Q , or to N/Q when 1 mole of gas is considered, without incurring any appreciable error; hence from equations (52.4) and (52.5), it is possible

to write

$$\frac{1}{B} \approx \frac{N}{Q} = \frac{Nh^3}{Q_i(2\pi mkT)^{3/2}V}, \quad (52.23)$$

and hence it is apparent that gas degeneration is to be expected for particles of small mass m , at low temperature T , and small volume V , i.e., at high pressure. The lightest gas known to obey the Bose-Einstein statistics is molecular hydrogen, and although this is a diatomic gas, it is of interest to see what deviations from ideal classical behavior due to gas degeneration might be expected according to equation (52.23). The boiling point of liquid hydrogen at atmospheric pressure, which is the lowest temperature at which the gas can exist at this pressure, is 20.38°K ., and so N/Q will be calculated at this temperature. Using the values for $N = 6.02 \times 10^{23}$, $h = 6.62 \times 10^{-27}$, $m = 2 \times 1.67 \times 10^{-24}$, $k = 1.38 \times 10^{-16}$, and 1,400 cc. for the molar volume V of hydrogen gas at its boiling point, and taking Q_i as unity, it is found that

$$\frac{1}{B} = 0.84 \times 10^{-2}$$

and hence

$$P = \frac{RT}{V} (1 - 1.49 \times 10^{-3})$$

for hydrogen gas at 20.38°K and 1 atm. pressure. The deviation due to gas degeneration is thus small, much smaller than the ordinary departure from ideal behavior due to intermolecular forces; it is thus impossible to observe the effect of gas degeneration of hydrogen at its normal boiling point. For most gases $1/B$ is less than 10^{-6} at ordinary temperatures and pressures, and hence the effect of degeneration would not be detectable.

There is some possibility that gas degeneration might be observed with helium, since this has only twice the molecular weight of hydrogen and can exist in the gaseous state at much lower temperatures. The boiling point at atmospheric pressure is 4.2°K , and the molar volume of the gas is 345 cc.; hence at this temperature

$$\frac{1}{B} = 0.134,$$

which is not very large. It is conceivable that the influence of Bose-Einstein statistics on gas degeneration might be observed at high pressures, but then normal deviations from classical behavior due to ordinary gas imperfection would greatly outweigh any effects due to degeneration. Another possibility is to decrease the temperature below the boiling point, but this would lower the pressure of the gas and hence reduce the extent of degeneration.

An examination of equations (52.16) and (52.22) shows that the internal energy and pressure of an ideal Bose-Einstein gas will both be less than for a classical ideal gas at the same temperature and volume. The reason for this can be seen from a study of the distribution law equation (52.1) for the Bose-Einstein statistics. For the higher energy levels, when $Be^{e/kT}$ is

large in comparison with unity, the number of molecules having energy in a given range will be the same as for classical statistics [equation (51.23)]. In the lower energy states, however, the presence of the -1 term in the denominator of equation (52.1) makes the number of molecules for a Bose-Einstein gas greater than for a gas obeying classical statistics. This means that the effect of the Bose-Einstein statistics is to increase the number of molecules in the lower energy levels; the decrease in the kinetic energy and pressure, as compared with classical behavior, can thus be understood.

The tendency for Bose-Einstein molecules to collect in the lower energy levels should be particularly marked under conditions of extreme degeneration, that is, at very low temperatures and high density (or pressure). Under these conditions, a phenomenon analogous to condensation, although not due to intermolecular attraction, might be expected. It has been suggested that the remarkable phenomena associated with the form of liquid helium known as helium II, which can apparently exist down to the absolute zero, provided the pressure does not exceed 25 atm., are to be ascribed to the behavior of a completely degenerate Bose-Einstein gas.³

52c. Bose-Einstein Statistics and Radiation.—There is one application of Bose-Einstein statistics that is of interest; it leads to the derivation of Planck's equation for the distribution of energy in black body radiation. It appears that radiation in thermal equilibrium, in a box with walls which do not absorb any of the radiation, may be treated as a system of elements, viz., photons, obeying the Bose-Einstein statistics. There is, however, an essential difference between such a system and those of the type previously considered. Although the energy remains constant, the total number of photons in the system is not independent of their distribution among the various possible energy states. The reason for this is to be found in the fact that the energy of the photon, according to the quantum theory, is equal to $h\nu$ where ν sec.⁻¹ is the frequency of the radiation; the exchange of a photon between two states of different frequency would thus result in an energy change. It is postulated, however, that the energy of the system remains constant; consequently there must be a change in the number of photons as the result of an interchange between different states. If the restriction $\sum \delta n_i = 0$ is no longer applicable, the term involving the undetermined multiplier α in the derivation of the Bose-Einstein (or other) distribution law does not enter into the argument; the final result, instead of equation (50.15), is then

$$n_i = \frac{g_i}{e^{\epsilon_i/kT} - 1}, \quad (52.24)$$

taking β as equal to $1/kT$. Writing $h\nu$ for the energy ϵ_i , this expression may be put in a form similar to equation (52.1); thus,

$$dn = \frac{g(d\nu)}{e^{h\nu/kT} - 1}. \quad (52.25)$$

³ London, *Phys. Rev.*, **54**, 947 (1938); *J. Phys. Chem.*, **43**, 49 (1939).

This is consequently the distribution law which may be applied to radiation, dn is the number of photons at equilibrium in the $g(d\nu)$ elementary eigenstates lying in the frequency range ν to $\nu + d\nu$.

Since radiation may be regarded as consisting of electromagnetic waves, the equation for the propagation is similar to that given in Section 4, namely

$$\frac{\partial^2 \phi}{\partial x^2} + \frac{\partial^2 \phi}{\partial y^2} + \frac{\partial^2 \phi}{\partial z^2} = \frac{1}{c^2} \cdot \frac{\partial^2 \phi}{\partial t^2}, \quad (52.26)$$

where c is the velocity of light. The radiation in the box under discussion can be regarded as consisting of standing waves, and hence a solution of this equation will be

$$\phi = \psi(x, y, z)(A \sin 2\pi\nu t + B \cos 2\pi\nu t), \quad (52.27)$$

where $\psi(x, y, z)$ is a function of the coordinates x, y, z only, and A and B are constants. Insertion of this solution into equation (52.26) leads to the result

$$\begin{aligned} \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} &= -\frac{4\pi^2\nu^2}{c^2} \psi \\ &= -\frac{4\pi^2\epsilon^2}{h^2c^2} \psi, \end{aligned} \quad (52.28)$$

since ϵ may be put equal to $h\nu$ by the quantum theory. The wave equation for photons thus becomes

$$-\frac{h^2c^2}{4\pi^2} \left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right) = \epsilon^2 \psi. \quad (52.29)$$

Treating the photon as a particle, in a cubical box of side l , with energy components in three directions parallel to the axes x, y, z , it is possible, by a procedure exactly analogous to that employed in Section 7, to derive the expression

$$\epsilon_x = \frac{hc}{2l} n_x$$

for the energy of the component in the x direction; similar equations hold for ϵ_y and ϵ_z . It follows, therefore, that the total energy ϵ will be given by

$$\epsilon = \frac{hc}{2l} r, \quad (52.30)$$

where the resultant quantum number r is defined by

$$r^2 = n_x^2 + n_y^2 + n_z^2.$$

Replacing ϵ in equation (52.30) by $h\nu$, and l by $V^{1/3}$, where V is the volume

of the cubical box, it is found that

$$r = 2V^{1/3} \frac{\nu}{c}. \quad (52.31)$$

By means of arguments parallel with those in Section 51b, the number of elementary eigenstates for systems with frequencies from zero to ν , is seen to be [cf. equation (51.14)]

$$\begin{aligned} g &= \frac{1}{8} \left(\frac{4}{3} \pi r^3 \right) \\ &= \frac{4}{3} \pi V \frac{\nu^3}{c^3}, \end{aligned}$$

and hence, by differentiation,

$$g(d\nu) = 4\pi V \frac{\nu^2}{c^3} d\nu, \quad (52.32)$$

for the number of eigenstates lying in the frequency range ν to $\nu + d\nu$. This result is not quite complete, however, since radiation of each frequency has two independent directions of polarization,⁴ it is necessary to multiply by two, giving

$$g(d\nu) = 8\pi V \frac{\nu^2}{c^3} d\nu. \quad (52.33)$$

Combining this expression with equation (52.25), which is the appropriate form of the Bose-Einstein distribution law, the result is

$$\frac{dn}{V} = \frac{8\pi\nu^2}{c^3} \cdot \frac{1}{e^{h\nu/kT} - 1} d\nu. \quad (52.34)$$

The left-hand side of equation (52.34) is the number of photons per unit volume, if this is multiplied by $h\nu$, the energy of a photon, the result is the energy per unit volume, i.e., the energy density, du , in the given frequency range; thus,

$$du = \frac{8\pi h\nu^3}{c^3} \cdot \frac{1}{e^{h\nu/kT} - 1} d\nu. \quad (52.35)$$

This is the Planck equation for the distribution of the energy density over the wave lengths (or frequencies) of black body radiation at a given temperature.

⁴ Radiation waves differ from sound or particle waves in the respect that they are transverse to the direction of propagation, and not longitudinal to it; hence any radiation wave must be regarded as due to the composition of two waves of the same period and phase, each polarized in one of two definite rectangular planes.

APPLICATIONS OF FERMI-DIRAC STATISTICS

53a. Fermi-Dirac Systems.—The distribution law derived from the Fermi-Dirac statistics is

$$n_i = \frac{g_i}{Be^{\epsilon_i/kT} + 1}, \quad (53.1)$$

and this may be put in the form

$$dn = \frac{g(d\epsilon)}{Be^{\epsilon/kT} + 1}, \quad (53.2)$$

where $g(d\epsilon)$ and B have the same significance as before. Using the value of $g(d\epsilon)$ given by equation (51.23), and introducing the additional degeneracy factor Q , it follows that for point masses with weak interaction

$$dn = \frac{2Q}{\pi^{1/2}} \cdot \frac{x^{1/2} dx}{Be^x + 1}, \quad (53.3)$$

where x is equal to ϵ/kT , and Q has the same significance as in equation (52.5); this is exactly analogous to equation (52.6) for the Bose-Einstein statistics, except that $+1$ replaces -1 , in the usual manner. Integration of equation (53.3) now gives

$$n = \frac{2Q}{\pi^{1/2}} \int_0^\infty \frac{x^{1/2} dx}{Be^x + 1} \quad (53.4)$$

and, further,

$$E = \frac{2kTQ}{\pi^{1/2}} \int_0^\infty \frac{x^{3/2} dx}{Be^x + 1}. \quad (53.5)$$

The evaluation of the integrals is again simplified if $B > 1$, but this is not a necessity for Fermi-Dirac statistics, as it was for the Bose-Einstein case; the value of α in the distribution equation (50.23) may be positive or negative without introducing any difficulties. If α is positive, so that B is greater than unity, the condition is referred to as *slight gas degeneration*; since the treatment is then quite similar to that used for the Bose-Einstein case, it will be given first. If $B > 1$, it is possible to write

$$(Be^x + 1)^{-1} = \frac{e^{-x}}{B} \left(1 - \frac{e^{-x}}{B} + \frac{e^{-2x}}{B^2} - \dots \right), \quad (53.6)$$

which is seen to be similar to the expression for $(Be^x - 1)^{-1}$, except that the signs of alternate terms in the parentheses on the right-hand side are changed. Without going through the details of the argument, it is readily found that for 1 mole of a monatomic Fermi-Dirac gas,

$$E = \frac{3}{2}RT \left(1 + \frac{1}{2^{5/2}B} - \frac{1}{3^{5/2}B^2} + \dots \right) \quad (53.7)$$

$$= \frac{3}{2}RT \left\{ 1 + \frac{1}{2^{5/2}} \left(\frac{N}{Q} \right) - \frac{1}{3^{5/2}} \left(\frac{N}{Q} \right)^2 + \dots \right\} \quad (53.8)$$

and

$$P = \frac{RT}{V} \left(1 + \frac{1}{2^{5/2}B} - \frac{1}{3^{5/2}B^2} + \cdots \right) \quad (53.9)$$

$$= \frac{RT}{V} \left\{ 1 + \frac{1}{2^{5/2}} \left(\frac{N}{Q} \right) - \frac{1}{3^{5/2}} \left(\frac{N}{Q} \right)^2 + \cdots \right\}, \quad (53.10)$$

where B is defined, as before, by equation (52.23), viz.,

$$\frac{1}{B} \approx \frac{N}{Q} = \frac{Nh^3}{Q_i(2\pi mkT)^{3/2}V}.$$

These equations give the total energy and pressure, respectively, under conditions of slight degeneration. Since the deviations from classical behavior are almost the same as for a Bose-Einstein gas, it is evident that there is little prospect of observing them even with molecular deuterium, the lightest substance, apart from electrons, for which the Fermi-Dirac statistics are applicable.

53b. Extreme Gas Degeneration.—At low temperatures the value of B may well become much less than unity; the condition of *extreme gas degeneration* will then arise. The results given in the previous section are then no longer satisfactory, and the evaluation of the integrals necessary to obtain expressions for the energy and the pressure of the monatomic Fermi-Dirac gas is much more difficult. It will be of interest to consider, in the first place, the special case of the absolute zero of temperature, i.e., at $T = 0$, for the treatment is then relatively simple, and the results are important. If B is assumed to be extremely small, or zero—as it will be at the absolute zero—then the term $Be^x + 1$ in the denominators of the integrands in equations (53.4) and (53.5) will be equal to unity; equation (53.4) may then be written as

$$n = \frac{2Q}{\pi^{1/2}} \int_0^{1/B} x^{1/2} dx, \quad (53.11)$$

where the upper limit of integration has been changed from ∞ to $1/B$, since B has been taken as zero. Carrying out the integration, the result is

$$\begin{aligned} n &= \frac{4Q}{3\pi^{1/2}} \cdot \frac{1}{B^{3/2}}, \\ \therefore \frac{1}{B} &= \left(\frac{3n\pi^{1/2}}{4Q} \right)^{2/3}. \end{aligned} \quad (53.12)$$

By equations (52.4) and (52.5),

$$Q = Q_i Q_i = Q_i \frac{(2\pi mkT)^{3/2}}{h^3} V,$$

and hence, by equation (53.12)

$$\frac{1}{B} = \frac{h^2}{2mkT} \left(\frac{3n}{4\pi V Q_i} \right)^{2/3}, \quad (53.13)$$

where V is the volume occupied by the n particles.

Just as equation (53.4) reduces to (53.11) in the special case of extreme gas degeneration, i.e., when B is virtually zero, so equation (53.5) becomes

$$E_0 = \frac{2kTQ}{\pi^{1/2}} \int_0^{1/B} x^{3/2} dx \quad (53.14)$$

$$= \frac{4kTQ}{5\pi^{1/2}} \cdot \frac{1}{B^{5/2}}, \quad (53.15)$$

the symbol E_0 being used because the energy is that for the absolute zero. Introducing the value for $1/B$ given by equation (53.13) into (53.15), the result is

$$E_0 = \frac{3nh^2}{10m} \left(\frac{3n}{4\pi V Q_i} \right)^{2/3} \quad (53.16)$$

It will be observed that both classical and Bose-Einstein statistics lead to a value of zero for the energy of a monatomic gas at the absolute zero. A Fermi-Dirac gas, however, possesses appreciable energy, i.e., zero-point energy, at this temperature. The expression for the zero-point energy of a highly degenerate Fermi-Dirac gas can be put in an alternative form that is of interest. According to equation (51.16) or (51.21), the number of eigenstates of a point mass with energy between ϵ and $\epsilon + d\epsilon$ is given by

$$g(d\epsilon) = Q_i \frac{4\pi m V}{h^2} (2m\epsilon)^{1/2} d\epsilon, \quad (53.17)$$

where Q_i has been introduced to allow for other degeneracy factors. The total number g^* of eigenstates with energy that does not exceed a specified value ϵ^* is then obtained by integration; thus,

$$\begin{aligned} g^* &= Q_i \frac{2\pi V}{h^2} (2m)^{3/2} \int_0^{\epsilon^*} \epsilon^{1/2} d\epsilon \\ &= Q_i \frac{4\pi V}{3h^2} (2m\epsilon^*)^{3/2}. \end{aligned} \quad (53.18)$$

At the absolute zero all the particles, e.g., electrons, will collect in the lowest possible energy states, but since the Fermi-Dirac statistics do not permit more than one element to each eigenstate, it follows that the number of elements is equal to the number of eigenstates.⁵ This result can be derived

⁵ The fact that two electrons can occupy the same orbital is due to the fact that they have opposite spins; this is allowed for by the degeneracy factor Q_i , which is two for electrons.

directly from equation (53.1); since B is zero at the absolute zero, it is evident that n_i is equal to g_i . It follows, therefore, that the value of g^* as given by equation (53.18) may be identified with n , the number of elements; hence,

$$n = Q_i \frac{4\pi V}{3h^3} (2m\epsilon^*)^{3/2}, \quad (53.19)$$

$$\therefore \epsilon^* = \frac{h^2}{2m} \left(\frac{3n}{4\pi V Q_i} \right)^{2/3}. \quad (53.20)$$

It is evident, therefore, by comparison with equation (53.13), that

$$\frac{\epsilon^*}{kT} = \frac{1}{B}, \quad (53.21)$$

and from equation (53.15),

$$E_0 = \frac{3}{5} n \epsilon^*. \quad (53.22)$$

The quantity ϵ^* is sometimes called the *Fermi energy*; it represents the energy of the highest level filled at the absolute zero, for the given system. The average energy per single particle, i.e., E_0/n , at the absolute zero is thus equal to three-fifths of the value for the particle of highest energy at this temperature, i.e., $\frac{3}{5}\epsilon^*$.

The Fermi-Dirac statistics, as already indicated, apply to electrons, and it is in fact in connection with the properties of the so-called "electron gas" (Section 53c) that these statistics have proved most useful. For electrons, Q_i is equal to 2, because of the two possible spin orientations; hence, equation (53.16) becomes

$$E_0 = \frac{3nh^2}{40m} \left(\frac{3n}{\pi V} \right)^{2/3}. \quad (53.23)$$

This gives the energy of a system of n electrons occupying a volume V at the absolute zero.

It has been seen earlier that the pressure P of any gas, irrespective of the type of statistics it obeys, is related to the energy E by the equation, $P = 2E/3V$, and hence for a Fermi-Dirac gas, using equation (53.22),

$$P_0 = \frac{2n}{5V} \epsilon^*, \quad (53.24)$$

for the pressure at the absolute zero. The behavior of a gas obeying the Fermi-Dirac statistics is thus quite different in this respect also from Bose-Einstein or classical gases. For the two latter, the pressure at the absolute zero of temperature should be zero, whereas for a Fermi-Dirac gas there should be an appreciable zero-point pressure.

At temperatures above the absolute zero, at which there is still considerable gas degeneration, i.e., E is still less than unity, the evaluation of the integrals presents some difficulties; methods have been devised, but as they

are complicated, the results only will be given here. The expression for the energy can be stated in the form of a series that converges rapidly at low temperatures, viz.,

$$E = \frac{3}{5}n\epsilon^* \left\{ 1 + \frac{5\pi^2}{12} \left(\frac{kT}{\epsilon^*} \right)^2 - \frac{\pi^4}{16} \left(\frac{kT}{\epsilon^*} \right)^4 + \dots \right\}, \quad (53.25)$$

which obviously reduces to equation (53.22) when T is zero. The pressure can be calculated from the energy in the usual manner.

It will be seen shortly that the heat capacity of an ideal Fermi-Dirac gas is important; this can be derived from equation (53.25) by making use of the familiar thermodynamic relationship, viz.,

$$\begin{aligned} C_V &= \left(\frac{\partial E}{\partial T} \right)_V \\ &= \frac{1}{2}nk\pi^2 \left(\frac{kT}{\epsilon^*} \right) \left\{ 1 - \frac{3\pi^2}{10} \left(\frac{kT}{\epsilon^*} \right)^2 + \dots \right\}. \end{aligned} \quad (53.26)$$

If the temperature is not too high, the quantity in the brackets may be set equal to unity so that

$$C_V = \frac{1}{2}nk\pi^2 \left(\frac{kT}{\epsilon^*} \right). \quad (53.27)$$

The heat capacity of a highly degenerate Fermi-Dirac gas at low temperatures is thus seen to be directly proportional to the absolute temperature.

53c. Electron Gas in Metals.—One of the most significant applications of Fermi-Dirac statistics is in connection with the theory of the metallic state; without entering into details, the basis of this theory is that a metal consists of a system of fixed positive nuclei and a number of mobile electrons, generally referred to as *electron gas*. There is no a priori method of estimating how many of the electrons in the metal may be regarded as free. For alkali metals, it is reasonable to suppose that there is one free electron for each atom, and this same assumption leads to satisfactory results for other metals. In the treatment of the electron gas in metals, it is postulated that the free electrons move in a field of uniform, constant potential energy. As long as the free electron remains in the "potential box," constituted by the metal, its potential energy will have this value, but in order to leave the box, that is, for the electron to be emitted from the metal, it must acquire additional energy.

Theoretically, the Fermi-Dirac statistics must, of course, apply to electrons, but it is of interest to see what the conditions are under which the classical statistics would represent an adequate approximation. Information in this connection can be obtained by calculating the value of B ; according to equation (53.13), B is given by

$$B = \frac{2mkT}{h^2} \left(\frac{4\pi VQ_i}{3n} \right)^{2/3}. \quad (53.28)$$

For electrons, the mass m is 9.1×10^{-28} , and Q_i is equal to 2, as seen above. Consider an average metal of atomic weight 100 and density 10; the volume V of 1 gram atom is 10 cc., and the number of atoms, and hence of electrons n , assuming one free electron for each atom, is 6.02×10^{23} . Under these conditions equation (53.28) gives

$$B = 1.5 \times 10^{-5} T.$$

It is at once evident that if B , i.e., e^a , is to be of the order of unity, so that the classical distribution might be applicable, the temperature would have to be extremely high. It is apparent, therefore, that at all reasonable temperatures, and especially at low temperatures, it is necessary to use the equations of the Fermi-Dirac statistics in connection with the study of the electron gas in metals.

A simple illustration of this fact is provided by a consideration of the contribution of electrons to the heat capacity of a metal; at all reasonable temperatures, this is given by equation (53.27), and remembering that kT/ϵ^* is equal to B [equation (53.31)], it follows that the electron heat capacity per gram atom of metal is then

$$(C_V)_{el.} = \frac{1}{2} R \pi^2 B, \quad (53.29)$$

where R is the molar gas constant. Utilizing the average (approximate) value of B derived above, it is found that

$$(C_V)_{el.} = 1.5 \times 10^{-4} T \text{ cal. per g. atom.} \quad (53.30)$$

At ordinary temperatures, viz., 300°K , the electron contribution to the atomic heat capacity of a metal will be about 0.05 cal.; this is very small, in comparison with the total heat capacity of more than 6 calories, and so there is little hope of observing the electronic heat capacity under these conditions. However, there is a possibility of investigating the effect of electron gas from studies of heat capacity at low temperatures. It will be shown in Section 54b, by means of the Debye theory of the specific heat of solids, that if the electronic contribution is ignored, the heat capacity of a solid element at very low temperatures should be proportional to T^3 . Subtracting the heat capacity calculated by the Debye equation from the observed value should give the heat capacity due to the electron gas. Data have been obtained in this manner for a number of metals at temperatures in the region of a few degrees above the absolute zero. The results are in general agreement with equation (53.30); in particular, the electronic contribution to the heat capacity has been found to be proportional to the absolute temperature, in agreement with expectation from the Fermi-Dirac statistics.

The pressure of the electron gas in a metal at the absolute zero may be calculated by means of equation (53.24); for an average metal, i.e., atomic weight 100 and density 10, this pressure is found to be of the order of 10^5 atm. At normal temperatures the pressure would be even higher. The

reason why the free electrons at these high pressures remain within the metal is because of the electrostatic attraction between the electrons and the fixed positive ions that constitute the crystal lattice.

53d. Thermionic Emission of Electrons from Metals.—It is not proposed to discuss in detail the properties of metals based on the concept of electron gas, but one particular aspect, namely that of *thermionic emission*, will be considered here as an illustration of the application of the Fermi-Dirac statistics to a problem of physical interest.

The translational energy ϵ_x , in the x direction, of a particle of mass m moving in a cubical box of side l , is given by equation (7.11), viz.,

$$\epsilon_x = \frac{h^2}{8ml^2} n_x^2, \quad (53.31)$$

where n_x is the appropriate quantum number. Further it was seen in Section 51b that n_x also gives the number of eigenstates with energy lying between zero and ϵ_x in the direction parallel to the x axis. Since the energy is entirely kinetic, it is possible to replace ϵ_x by $p_x^2/2m$, where p_x is the x component of the momentum; making this substitution, equation (53.31) yields

$$\begin{aligned} p_x^2 &= \frac{h^2}{4l^2} n_x^2, \\ \therefore n_x &= \frac{2l}{h} p_x. \end{aligned} \quad (53.32)$$

It should be noted that in these equations p_x is actually the absolute, i.e., numerical, value of the x component of the momentum, irrespective of its sign.

In view of the significance of n_x with respect to the eigenstates of the energy, it can also be regarded as giving the number of quantum states with absolute values of the x component of the momentum between zero and p_x . It follows, therefore, from equation (53.32), that the number of eigenstates $g(dp_x)$ within the momentum range of p_x to $p_x + dp_x$ may be represented by

$$g(dp_x) = \frac{2l}{h} dp_x. \quad (53.33)$$

The number of eigenstates in the range $dp_x dp_y dp_z$, i.e., in the element of momentum space having this extension, would be

$$g(dp) = \frac{8l^3}{h^3} dp_x dp_y dp_z. \quad (53.34)$$

So far no account has been taken of the degeneracy of the energy states due to other causes, such as spin; for electrons, which are now being considered, it is necessary to multiply by two, as seen above; hence, equation (53.34)

becomes

$$g(dp) = \frac{16V}{h^3} dp_x dp_y dp_z, \quad (53.35)$$

where l^3 has been replaced by V , the volume of the container.

It has been mentioned that the terms dp_x , etc., refer to absolute values, irrespective of sign; it is now required to take the sign of the momentum into account, since in the subsequent treatment it is necessary for the components of the momentum of the various electrons to have the same sign. For this purpose, it may be supposed that half the total number of electrons have positive p_x , while the other half have negative p_x ; the same assumption may also be made for the components p_y and p_z . The number of eigenstates will then be one-eighth as many as that given by equation (53.35); thus, for the present purpose, it is possible to write

$$g(dp) = \frac{2V}{h^3} dp_x dp_y dp_z. \quad (53.36)$$

Introducing this result into the Fermi-Dirac distribution law equation (53.2), gives

$$dn = \frac{2V}{h^3} \cdot \frac{1}{Be^{\epsilon/kT} + 1} dp_x dp_y dp_z$$

for the number of electrons in the volume V , each having a total kinetic energy ϵ , and momenta within the specified range. The corresponding number in unit volume is then

$$dn = \frac{2}{h^3} \cdot \frac{1}{Be^{\epsilon/kT} + 1} dp_x dp_y dp_z. \quad (53.37)$$

The number of electrons $n(dp_x)$, with the x component of momentum in the range dp_x , that are incident in unit time on a unit area normal to the x axis is obtained by integrating equation (53.37) over all possible values of p_y and p_z .⁶ This gives the number of electrons in unit volume, that satisfy the specified conditions, and the result must be multiplied by the speed of the electrons, p_x/m , in the x direction; thus,

$$n(dp_x) = \frac{2}{h^3 m} p_x dp_x \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{1}{Be^{\epsilon/kT} + 1} dp_y dp_z. \quad (53.38)$$

The total kinetic energy ϵ of the electrons can be represented by

$$\epsilon = \frac{1}{2m} (p_x^2 + p_y^2 + p_z^2),$$

⁶ This is equivalent to integrating over the limits of p_x and $p_x + dp_x$ for the variable p_x , but for p_y and p_z the limits are $-\infty$ to ∞ .

and if the quantity p_ρ^2 is defined by

$$p_\rho^2 = p_v^2 + p_z^2,$$

it follows that

$$\epsilon = \frac{1}{2m} (p_z^2 + p_\rho^2). \quad (53.39)$$

Making this substitution in equation (53.38), and at the same time changing the variables, the result obtained is

$$n(dp_x) = \frac{4\pi}{h^3 m} p_x dp_x \int_0^\infty \frac{1}{B e^{(p_z^2 + p_\rho^2)/2mkT} + 1} p_\rho dp_\rho,$$

and on evaluation of the integral, it is found that

$$n(dp_x) = \frac{4\pi kT}{h^3} \ln \left(\frac{e^{-p_x^2/2mkT}}{B} + 1 \right) p_x dp_x. \quad (53.40)$$

The kinetic energy in the x direction is given by

$$\epsilon_x = \frac{p_x^2}{2m},$$

$$\therefore m d\epsilon_x = p_x dp_x.$$

The number $n(d\epsilon_x)$ of electrons, with kinetic energy in the range ϵ_x to $\epsilon_x + d\epsilon_x$, striking the surface referred to above, is then obtained from equation (53.40) as

$$n(d\epsilon_x) = \frac{4\pi mkT}{h^3} \ln \left(\frac{e^{-\epsilon_x/kT}}{B} + 1 \right) d\epsilon_x. \quad (53.41)$$

According to equation (53.21), $1/B$ is equal to ϵ^*/kT , where ϵ^* is the so-called Fermi energy, for a highly degenerate gas at very low temperatures. For the present problem, however, it is possible to write as a rough approximation

$$e^{\epsilon^*/kT} \approx \frac{1}{B},$$

and introduction of this result into equation (53.41) gives

$$n(d\epsilon_x) = \frac{4\pi mkT}{h^3} \ln \{ e^{-(\epsilon_x - \epsilon^*)/kT} + 1 \} d\epsilon_x. \quad (53.42)$$

If the quantity $\epsilon_x - \epsilon^*$ is large in comparison with kT , all terms beyond the first may be neglected in the expansion of the logarithm in the form of a power series, i.e., $\ln(x + 1) \approx x$, if x is small; hence,

$$n(d\epsilon_x) = \frac{4\pi mkT}{h^3} e^{-(\epsilon_x - \epsilon^*)/kT} d\epsilon_x. \quad (53.43)$$

It will now be supposed that the electrons under consideration constitute the electron gas in a metal; equation (53.43) then gives the number of these electrons coming from the inside of the metal that are incident on unit area of its surface in unit time with kinetic energy, normal to the surface, lying in the range ϵ_z to $\epsilon_z + d\epsilon_z$. If η is the work required to take a single electron from rest inside the metal and bring it outside the metal, also in a state of rest, the number of electrons Z striking the surface of the metal, from inside, that succeed in escaping is given by

$$\begin{aligned} Z &= \int_{\eta}^{\infty} n(d\epsilon_z) \\ &= \frac{4\pi mkT}{h^3} \int_{\eta}^{\infty} e^{-(\epsilon_z - \epsilon^*)/kT} d\epsilon_z \\ &= \frac{4\pi mk^2 T^2}{h^3} e^{-(\eta - \epsilon^*)/kT}. \end{aligned} \quad (53.44)$$

The Fermi energy ϵ^* is the energy of an electron in the highest occupied level in the metal, at the absolute zero; hence, the quantity $\eta - \epsilon^*$ which appears in the exponential term in equation (53.44) may be regarded, approximately, as the average energy required to remove an electron from the interior of the metal, at constant temperature and volume, and bring it to rest outside the metal. This energy quantity, which may be given the symbol χ , and is generally expressed in electron-volts, is known as the *thermionic work function*; making this substitution of χ for $\eta - \epsilon^*$ in equation (53.44), the latter becomes

$$Z = \frac{4\pi mk^2 T^2}{h^3} e^{-\chi/kT}. \quad (53.45)$$

This expression gives the rate at which electrons leave unit area of a metal, as a function of temperature; it is, therefore the equation for the phenomenon of *thermionic emission*. In practice, the emission is measured as the current flowing from unit area of the heated metal to a collecting electrode; the magnitude of the current I is obtained by multiplying the number of electrons leaving unit area of the surface in unit time by the electronic charge e ; thus,

$$I = Ze = \frac{4\pi mk^2 e}{h^3} T^2 e^{-\chi/kT} \quad (53.46)$$

$$= AT^2 e^{-\chi/kT}, \quad (53.47)$$

where A is a universal constant. This result is identical in form with the empirical Richardson equation for thermionic emission.

If the magnitude of the constant A is evaluated, it is found that it should, theoretically, be equal to 120 in amp. cm.⁻² deg.⁻² units. Experimental observation, however, has led in a number of reliable cases to a figure of

approximately $60 \text{ amp. cm.}^{-2} \text{ deg.}^{-2}$, and several explanations have been proposed to account for the discrepancy. It will be noted, in the first place, that in the derivation of equation (53.46) the tacit assumption was made that every electron reaching the surface of the metal from the interior with energy in excess of the amount η would actually succeed in escaping. It is possible, however, that some of the electrons, which theoretically have sufficient energy to permit their escape, are reflected at the surface; the result obtained in equation (53.46) should thus be multiplied by a *transmission coefficient*, equal to the fraction of the electrons reaching the surface that are not reflected. According to the experimental results, this transmission coefficient should have a value of about 0.5 in several cases, although quantum mechanical calculations indicate that a figure much closer to unity is to be expected. Another possibility is that the thermionic work function is not independent of temperature, as is assumed in the calculation of the value of A from the experimental results. Such a temperature variation, if not allowed for, would influence the apparent magnitude of A .

It is of interest to note that the thermionic emission equation (53.46) can be derived in an alternative manner which will be described more fully in Section 55e. If the electrons are allowed to escape from the metal into an enclosed space, when equilibrium is attained the rate at which electrons leave the metal surface, as calculated above, should be equal to the rate at which they return to the metal from the vapor phase. The density of electrons in the latter phase is so low that in spite of the small mass of the electron, the Fermi-Dirac statistics reduce to the classical form. It will be seen that under these conditions the calculation of the rate at which electrons return to the metal is quite simple.

HEAT CAPACITY OF SOLIDS -

54a. The Solid State.—Apart from a relatively few cases, referred to in the previous sections, in which it is essential to use the distribution equations derived from the Bose-Einstein or Fermi-Dirac statistics, it is possible to use the classical statistics without causing any appreciable error. However, it is generally necessary, except for translational energy, to allow for the fact that the energy of a molecule is quantized and is not continuously variable. This point may be illustrated by a discussion of the atomic heats of solid elements; in accordance with the conclusion already reached, it will be assumed that the electronic contribution to the heat capacity can be neglected at ordinary temperatures.

An ideal solid may be regarded as consisting of a space lattice of independent atoms vibrating about their respective equilibrium positions, but not interacting with one another in any way. If the vibration is strictly harmonic in character, the energy can be expressed as the sum of two square terms; hence, according to the principle of the equipartition of energy, the internal energy will be equal to kT per atom for each vibrational mode (cf. Section 49c). Since the atoms will be free to oscillate in all directions

in space, each atom may be supposed to have three vibrational degrees of freedom, i.e., three vibrational modes; the internal energy should thus be $3kT$ per atom, or $3NkT$, i.e., $3RT$, per g. atom, i.e.,

$$E = 3RT. \quad (54.1)$$

Differentiation with respect to temperature at constant volume gives C_V , the atomic heat capacity at constant volume; hence,

$$C_V = \left(\frac{\partial E}{\partial T} \right)_V = 3R. \quad (54.2)$$

The atomic heat of an ideal solid should thus be $3R$, i.e., 5.96 cal., independent of temperature. It is true, as exemplified by the empirical law of Dulong and Petit, that many elements do have atomic heats in the vicinity of 6.0 cal., but certain elements, particularly some of those with low atomic weights, have atomic heats that are appreciably less than this value. Further, the atomic heats are not independent of temperature, as they should be according to equation (54.2). 6.0

The first step in the improvement of the theory of the heat capacity of solid elements was taken by Einstein,⁷ who applied the quantum theory to calculate the energy of the atomic oscillators, instead of using the classical equipartition value. The treatment as given below has been somewhat modernized by utilizing the results derived from the wave mechanics. It was seen in Section 8 that the energy ϵ_v of a harmonic oscillator of frequency ν may be expressed by the relationship

$$\epsilon_v = \left(v + \frac{1}{2} \right) h\nu, \quad (54.3)$$

where the frequency ν is here expressed in sec^{-1} ; the vibrational quantum number v may be 0, 1, 2, etc. Except when degenerate frequencies occur in polyatomic molecules, there is one eigenstate for each value of the vibrational energy; in this case, therefore, each vibrational quantum number corresponds to one eigenstate. The Maxwell-Boltzmann distribution equation

$$n_i = \frac{g_i}{B e^{\epsilon_i/kT}}$$

now takes the form

$$n_v = \frac{1}{B} e^{-\epsilon_v/kT} \quad (54.4)$$

where n_v is the number of oscillators in the quantum state (eigenstate) of energy ϵ_v at the temperature T . The total number N of oscillators in the system is obtained by summing all the terms of the type given by equation

⁷ Einstein, *Ann. Physik*, 22, 180 (1907).

(54.4), for all integral values of v from zero to infinity; thus,

$$N = \frac{1}{B} \sum_{v=0}^{\infty} e^{-\epsilon_v/kT}. \quad (54.5)$$

The energy of all the oscillators in each eigenstate is equal to the product of the number of oscillators n_v in that state by their energy ϵ_v ; hence, the total vibrational energy E of the system of N oscillators will be given by

$$E = \sum_{v=0}^{\infty} \epsilon_v n_v = \frac{1}{B} \sum_{v=0}^{\infty} \epsilon_v e^{-\epsilon_v/kT}. \quad (54.6)$$

The mean energy $\bar{\epsilon}$ for a single oscillator in the given system is equal to the total energy E divided by the total number N of molecules; hence by equations (54.5) and (54.6)

$$\bar{\epsilon} = \frac{E}{N} = \frac{\sum \epsilon_v e^{-\epsilon_v/kT}}{\sum e^{-\epsilon_v/kT}}. \quad (54.7)$$

Introducing the value of ϵ_v given by equation (54.3), this becomes

$$\begin{aligned} \bar{\epsilon} &= \frac{\sum (v + \frac{1}{2}) e^{-(v+\frac{1}{2})h\nu/kT}}{\sum e^{-(v+\frac{1}{2})h\nu/kT}} h\nu \\ &= \frac{\sum v e^{-vh\nu/kT}}{\sum e^{-vh\nu/kT}} h\nu + \frac{h\nu}{2} \\ &= \frac{h\nu}{e^{h\nu/kT} - 1} + \frac{h\nu}{2}. \end{aligned} \quad (54.8)$$

(It may be remarked that the last term in equation (54.8), i.e., $\frac{1}{2}h\nu$, did not appear in Planck's original calculation for the mean energy of a linear oscillator; it is the zero-point energy which arises from quantum mechanical considerations.)

An atom in a crystal may be regarded as a three-dimensional oscillator, and hence the internal energy E per gram atom, consisting of N such oscillators, is equal to $3N\bar{\epsilon}$; consequently,

$$E = 3N \frac{h\nu}{e^{h\nu/kT} - 1} + \frac{3}{2}Nh\nu. \quad (54.9)$$

The Einstein atomic heat equation is then obtained by differentiation of equation (54.9) with respect to temperature in the usual manner; thus

$$C_V = \left(\frac{\partial E}{\partial T} \right)_V = 3Nk \left(\frac{h\nu}{kT} \right)^2 \frac{e^{h\nu/kT}}{(e^{h\nu/kT} - 1)^2}. \quad (54.10)$$

According to this relationship C_V should approach zero at very low temperatures, whereas at high temperatures, when $h\nu/kT$ is small in comparison with unity, the expression reduces to $3Nk$, i.e., $3R$, in agreement with the classical treatment, based on the equipartition principle, and the law of Dulong and

Petit. Although these conclusions are in general accord with experiment, and the Einstein equation represented an important advance, it did not completely solve the problems of atomic heat.

54b. The Debye Specific Heat Equation.—Owing to the proximity of the atoms in a crystal, it is very improbable they will act as independent units oscillating with the same frequency. As a result of interactions, the atoms will execute complex vibrations, but these can be treated as made up of a series of simple harmonic motions with various frequencies. A solid containing N atoms will thus behave as a system of $3N$ coupled harmonic oscillators, and there will be a total of $3N$ different frequencies.⁸ The lowest frequency will be zero, but there is a definite limit to the highest frequency; this maximum, designated by ν_m , arises when the wave length of the oscillations is of the same order as the interatomic distances.

In order to determine the distribution of frequencies, Debye⁹ disregarded the atomic structure of the solid, and treated it as a homogeneous, isotropic, elastic medium; the vibrations of the atoms may thus be treated as equivalent to elastic waves, of the type of sound waves, propagated through this continuous medium. These waves may be considered as made up of three waves propagated in directions at right angles; they are the longitudinal wave in the direction of motion, and two equivalent transverse waves. It can be shown by the theory of elasticity that for elastic waves moving in a solid of volume V , the number of modes of vibration dn , with frequencies in one direction lying in the range between ν and $\nu + d\nu$, is given by the expression

$$dn = 4\pi V \frac{\nu^2}{c^3} d\nu, \quad (54.11)$$

where c is the velocity of the waves. It will be noted that this equation is identical in form with equation (52.32) for the number of eigenstates of radiation lying in a given frequency range. The longitudinal wave has a velocity of c_l , while the two transverse waves have a velocity of c_t ; hence the number of vibrations in the frequency range ν to $\nu + d\nu$ in three directions, is given by

$$dn = 4\pi V \left(\frac{1}{c_l^3} + \frac{2}{c_t^3} \right) \nu^2 d\nu. \quad (54.12)$$

It has been mentioned previously that the total number of vibrational frequencies in the solid containing N atoms is $3N$; hence, integration of

⁸ Since the atoms in the crystal are now no longer independent, the whole crystal may perhaps be regarded as a large molecule; it would then be more exact to say that the system has $3N - 6$ degrees of vibrational freedom. However, since N is large, there is no appreciable error incurred in using $3N$ instead of $3N - 6$.

The application of the distribution laws for weakly interacting particles, derived in the present chapter, to such a crystalline solid is justified, for it can be shown that the system of N atoms, whose positions are fixed in space, is equivalent to $3N$ independent oscillators (cf. Section 67c).

⁹ Debye, *Ann. Physik*, 39, 789 (1912); see also, Lewis and Gibson, *J. Am. Chem. Soc.*, 39, 2554 (1917).

equation (54.12) over the frequency limits of zero to the maximum ν_m should give the value $3N$, i.e.,

$$\begin{aligned} 3N &= 4\pi V \left(\frac{1}{c_l^3} + \frac{2}{c_t^3} \right) \int_0^{\nu_m} \nu^2 d\nu \\ &= \frac{4\pi V}{3} \left(\frac{1}{c_l^3} + \frac{2}{c_t^3} \right) \nu_m^3, \\ \therefore \left(\frac{1}{c_l^3} + \frac{2}{c_t^3} \right) &= \frac{9N}{4\pi V \nu_m^3}. \end{aligned} \quad (54.13)$$

Insertion of this result into equation (54.12) then gives

$$dn = 9N \frac{\nu^2}{\nu_m^3} d\nu \quad \text{[Sketch of a sawtooth wave with a peak and a trough]} \quad (54.14)$$

for the number of modes of vibration, in three directions, in the frequency range ν to $\nu + d\nu$. If this value of dn is multiplied by the mean energy of an oscillator as given by equation (54.8), and the product integrated over the frequency range from zero to ν_m , the result will give the total internal energy E of the N atoms; thus,

$$E = \frac{9N}{\nu_m^3} \int_0^{\nu_m} \left(\frac{h\nu}{e^{h\nu/kT} - 1} + \frac{h\nu}{2} \right) \nu^2 d\nu. \quad (54.15)$$

A quantity called the *characteristic temperature*, or the *Debye temperature*, of the solid under consideration is given the symbol θ , and is defined by

$$\theta = \frac{h\nu_m}{k}, \quad (54.16)$$

and the variable ν is replaced by the dimensionless variable x , defined by

$$x = \frac{h\nu}{kT}. \quad (54.17)$$

The energy equation (54.15) can now be written in the form

$$E = 9NkT \left(\frac{T}{\theta} \right)^3 \int_0^{\theta/T} \frac{x^3}{e^x - 1} dx + \frac{9Nk}{8} \theta, \quad (54.18)$$

where the last term is the result of integrating out the zero-point energy contribution in equation (54.8). Differentiation of equation (54.18) with respect to the temperature then gives

$$C_V = 3Nk \left\{ 12 \left(\frac{T}{\theta} \right)^3 \int_0^{\theta/T} \frac{x^3}{e^x - 1} dx - \frac{3}{e^{\theta/T} - 1} \cdot \frac{\theta}{T} \right\}. \quad (54.19)$$

The evaluation of the integral in equations (54.18) and (54.19) is achieved

by expressing the integrand in the form of an infinite series, and integrating term by term. If the temperature is moderate or relatively high, then

$$\left(\frac{T}{\theta}\right)^3 \int_0^{\theta/T} \frac{x^3}{e^x - 1} dx = \frac{1}{3} - \frac{1}{8} \left(\frac{\theta}{T}\right) + \frac{1}{60} \left(\frac{\theta}{T}\right)^2 - \frac{1}{5040} \left(\frac{\theta}{T}\right)^4 + \dots,$$

and by equation (54.18),

$$E = 3NkT \left\{ 1 + \frac{1}{20} \left(\frac{\theta}{T}\right)^2 - \frac{1}{1680} \left(\frac{\theta}{T}\right)^4 + \dots \right\}. \quad (54.20)$$

On differentiation with respect to T , it is seen that

$$C_V = 3Nk \left\{ 1 - \frac{1}{20} \left(\frac{\theta}{T}\right)^2 + \frac{1}{560} \left(\frac{\theta}{T}\right)^4 - \dots \right\}. \quad (54.21)$$

At high temperatures, it is apparent that the atomic heat capacity should approach the classical value of $3R$.

At low temperatures, x is large and the integration can then be carried out in an alternative form; the result is

$$\left(\frac{T}{\theta}\right)^3 \int_0^{\theta/T} \frac{x^3}{e^x - 1} dx = \frac{\pi^4}{15} \left(\frac{T}{\theta}\right)^3 - e^{-\theta/T} - f \left\{ \left(\frac{T}{\theta}\right) e^{-\theta/T} \right\},$$

where the last term on the right-hand side represents a function that decreases rapidly with decreasing temperature. For most purposes this, as well as $e^{-\theta/T}$, can be neglected at low temperatures; the expression for the energy then becomes

$$E = 3NkT \left\{ \frac{\pi^4}{15} \left(\frac{T}{\theta}\right)^3 - \dots \right\} + \frac{9Nk}{8} \theta, \quad (54.22)$$

and hence,

$$C_V = 3Nk \left\{ \frac{4}{5} \pi^4 \left(\frac{T}{\theta}\right)^3 - \dots \right\}. \quad (54.23)$$

A number of interesting conclusions can be drawn from the foregoing equations (54.21) and (54.23), for the heat capacity. In the first place, it is evident that C_V is a function of the quantity θ/T only; hence the plot of C_V against T/θ should yield a curve that is the same for all solid elements. The nature of the curve is shown in Fig. 40, and it is an experimental fact that the heat capacities of many elements, and even of a few simple compounds that crystallize in the cubic system, have been found to fall on, or very close to, this universal curve.

In order to verify the applicability of the Debye equation to a given solid it is, of course, necessary to know the value of the characteristic temperature θ ; this is generally derived from a measurement of the heat capacity C_V at any convenient temperature T , preferably on the rising part of the Debye curve (Fig. 40). By means of this curve the value of T/θ correspond-

ing to the experimental C_V can be obtained, and hence θ can be derived, since T is known. Utilizing this result for θ , the experimental heat capacities at various temperatures can be plotted against T/θ to see if they fall on the theoretical curve.

Another way of testing the Debye relationship is to use the curve, or the equivalent tables giving C_V as a function of T , which are to be found in

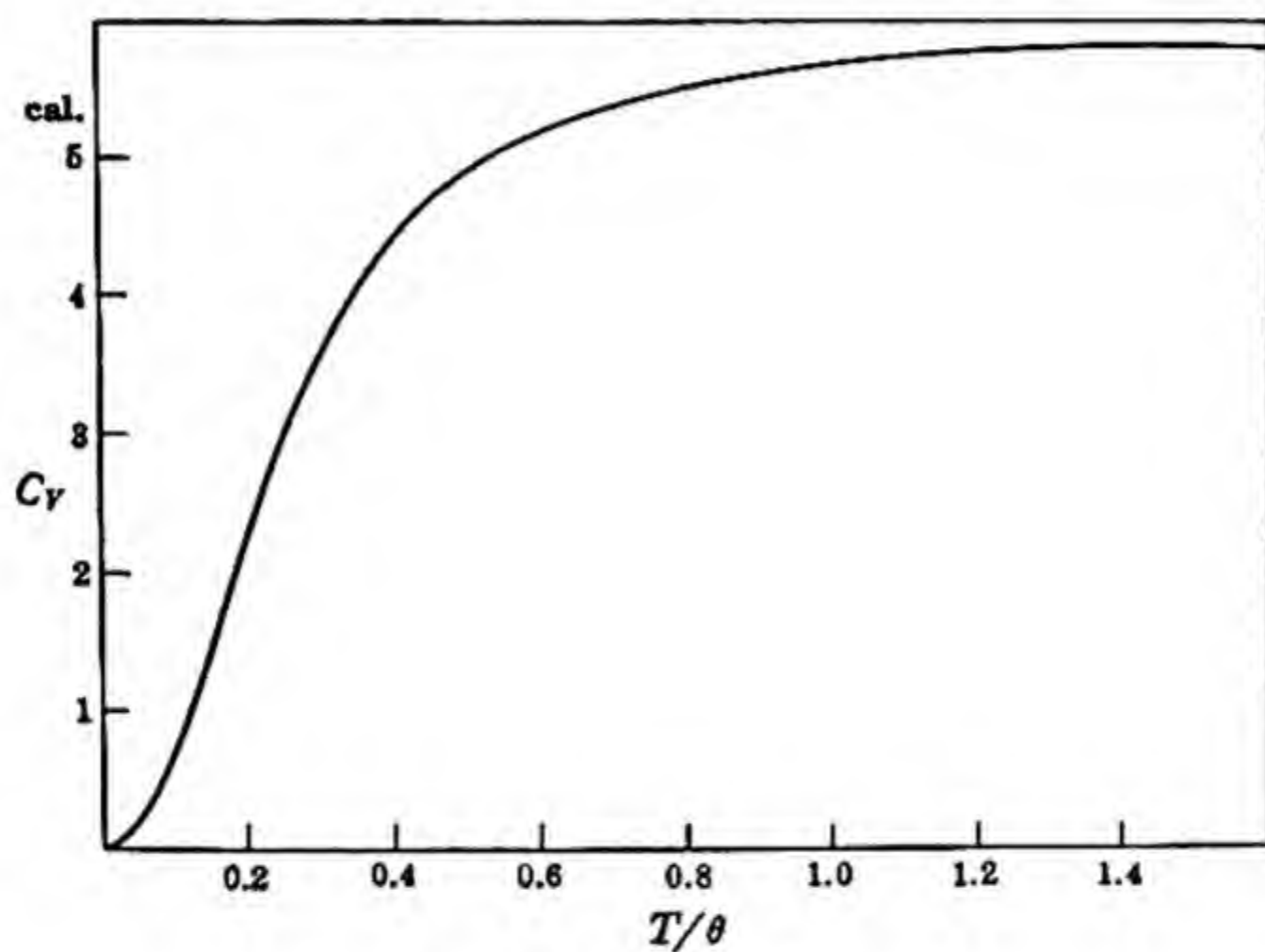


FIG. 40. Debye specific heat curve

many reference works, to calculate θ from heat capacity data at a series of temperatures. If the Debye equation is applicable, then the values of θ will be constant for a given element. In actual fact, slight variations have been found, but these are small and are attributed to the approximation of treating a crystalline solid as a continuous medium in order to determine the distribution of vibration frequencies.

According to equation (54.13), the maximum frequency ν_m is related to the velocities of longitudinal and transverse waves, e.g., sound waves, in the crystal; further, since the characteristic temperature θ is equal to $h\nu_m/k$, by definition [equation (54.16)], it is apparent that there will be a connection between θ and the velocities c_l and c_t . This is readily found to be

$$\frac{1}{\theta^3} = \frac{4\pi V k^3}{9Nh^3} \left(\frac{1}{c_l^3} + \frac{2}{c_t^3} \right). \quad (54.24)$$

According to the theory of elasticity, the velocities are related to the compressibility κ , Poisson's ratio σ , and the density ρ of the crystal, by means of the expressions

$$c_l^2 = \frac{3(1 - \sigma)}{(1 + \sigma)\kappa\rho} \quad \text{and} \quad c_t^2 = \frac{3(1 - 2\sigma)}{2(1 + \sigma)\kappa\rho}. \quad (54.25)$$

Hence, if the elastic constants of the solid are known, it should be possible to calculate the characteristic temperature θ ; this has been done in a number of cases, and some of the results obtained, compared with those derived from heat capacity data, are recorded in Table XVIII. The agreement is seen to be very satisfactory.

TABLE XVIII. CHARACTERISTIC TEMPERATURES FROM ELASTIC CONSTANTS AND FROM HEAT CAPACITIES

Element	ρ	κ	σ	θ (calc.)	θ (from C_V)
Al	2.71	1.36	0.337	398	402
Cu	8.96	0.74	0.334	315	332
Ag	10.53	0.92	0.379	215	214
Pb	11.32	2.0	0.446	88	73

Attention may now be paid to equation (54.23) giving the heat capacity of a solid at low temperatures; neglecting all terms beyond the first, this becomes

$$C_V = \frac{12}{5} R \pi^4 \left(\frac{T}{\theta} \right)^3$$

$$= 464.4 \left(\frac{T}{\theta} \right)^3 \text{ cal.} \quad (54.26)$$

The important conclusion is therefore to be drawn from the Debye theory that at low temperatures the atomic heat capacity of an element should be proportional to T^3 , and it should become zero at the absolute zero. In order for equation (54.26) to hold, it is necessary that the temperature should be less than $\theta/10$; this means that for most substances the experimental temperatures must be below about 20° K. Heat capacity measurements made at sufficiently low temperatures have served to confirm the reliability of the T^3 relationship for a number of elements and compounds. The proportionality of heat capacities to the third power of the absolute temperature at low temperatures has been found of great value for the purpose of extrapolating heat capacities to the absolute zero; such extrapolations are important in connection with the experimental determination of entropies from thermal data. It may be noted, incidentally, that the slope of the plot of C_V against T^3 , which should be equal to $464.4/\theta^3$ at very low temperatures, provides an alternative method for deriving the characteristic temperature.

Further reference to the Debye theory of specific heats of solids will be made in Section 67c.

CHAPTER VIII

STATISTICAL THERMODYNAMICS ¹

THERMODYNAMICS AND STATISTICS

55a. Entropy and Probability.—One of the most important aspects of statistical mechanics, from the standpoint of the physical chemist, is its correlation with thermodynamics, especially with the second and third laws. The most convenient approach to this problem is through the concept of entropy. It is known from thermodynamics that when a system, with constant volume and energy, is in equilibrium the entropy is a maximum; on the other hand, according to statistical mechanics such a system is in equilibrium when the total probability is a maximum. It appears, therefore, as suggested by Boltzmann, that there should be a relationship between entropy and probability. The (thermodynamic) probability may be defined in accordance with earlier discussion as the number of microscopic states, or complexions, corresponding to the given macroscopic state. The connection between entropy and probability may be expressed as $S = f(W)$, where S is the entropy and W is the probability. The nature of the function $f(W)$ can be ascertained by considering two systems having entropies S_1 and S_2 , and probabilities W_1 and W_2 respectively. Since entropy is an extensive property, the entropy S_{12} of the combined system is equal to the sum $S_1 + S_2$; the probability W_{12} of this system is, however, the product $W_1 \times W_2$, so that since

$$\begin{aligned} S_{12} &= f(W_{12}), \\ \therefore S_{12} &= S_1 + S_2 = f(W_1 \times W_2). \end{aligned} \quad (55.1)$$

For the two individual systems, $S_1 = f(W_1)$ and $S_2 = f(W_2)$, and hence it follows that

$$f(W_1 \times W_2) = f(W_1) + f(W_2). \quad (55.2)$$

It is evident that in order to satisfy equations (55.1) and (55.2) it is necessary that

$$S = k \ln W + \text{constant}, \quad (55.3)$$

where k is a constant, which can be shown to be identical with the familiar Boltzmann constant, that is, the gas constant per single molecule, R/N . It was postulated by Planck that the additional constant in equation (55.3)

¹ Aston, Chapter IV in "A Treatise on Physical Chemistry," Vol. I, Edited by Taylor and Glasstone; Fowler and Guggenheim, "Statistical Thermodynamics"; Mayer and Mayer, "Statistical Mechanics"; Tolman, "The Principles of Statistical Mechanics."

be taken as zero, thus yielding the relationship

$$S = k \ln W \quad (55.4)$$

between the entropy and the so-called thermodynamic probability.

55b. Entropy and Number of Eigenstates.—For the purpose of relating thermodynamics to quantum statistics, it is more satisfactory to define the entropy of a system in terms of the corresponding number of quantum states, i.e., eigenstates. If the number of eigenstates for two independent systems are G_1 and G_2 , then the number G_{12} of eigenstates for the combined system will be given by

$$G_{12} = G_1 \times G_2, \quad (55.5)$$

since for every one of the G_1 eigenstates in the system 1 there will be G_2 different eigenstates in the system 2, making a total of $G_1 \times G_2$ states. It follows, therefore, in accordance with the remarks in the previous paragraph, that the entropy may be treated as a logarithmic function of the number of eigenstates. Suppose a property S of a given system is defined by the equation

$$S = k \ln G, \quad (55.6)$$

where k is a constant having the dimensions of energy per degree; since G is merely a number, and hence is dimensionless, it follows that S will have the dimensions of entropy, i.e., energy per degree. It will be shown presently that S has the properties of thermodynamic entropy, and by the proper choice of the constant k it can, in fact, be made identical with entropy.

The number of eigenstates for a specified distribution of n elements depends on the type of statistics; the required numbers are given by equations (50.7) and (50.17) for the Bose-Einstein and Fermi-Dirac statistics, respectively. By the use of the Stirling approximation, the corresponding values of $\ln G$ are found to be as follows [cf. equations (50.10) and (50.19)]:

Bose-Einstein statistics.

$$\begin{aligned} \ln G &= \sum_i \{ (n_i + g_i) \ln (n_i + g_i) - n_i \ln n_i - g_i \ln g_i \} \\ &= \sum_i \left\{ n_i \ln \left(1 + \frac{g_i}{n_i} \right) + g_i \ln \left(1 + \frac{n_i}{g_i} \right) \right\}. \end{aligned} \quad (55.7)$$

Fermi-Dirac statistics.

$$\begin{aligned} \ln G &= \sum_i \{ (n_i - g_i) \ln (g_i - n_i) - n_i \ln n_i + g_i \ln g_i \} \\ &= \sum_i \left\{ n_i \ln \left(\frac{g_i}{n_i} - 1 \right) - g_i \ln \left(1 - \frac{n_i}{g_i} \right) \right\}. \end{aligned} \quad (55.8)$$

If the conditions are such that classical statistics can be applied, then g_i must be considerably greater than n_i , i.e., $g_i/n_i \gg 1$; it can be readily seen

that under these conditions both equations (55.7) and (55.8) reduce to the same form, namely,

$$\ln G = \sum_i (n_i \ln g_i - n_i \ln n_i + n_i). \quad (55.9)$$

The corresponding equation for $\ln G$ in the Maxwell-Boltzmann statistics, obtained by taking logarithms of equation (50.25) and applying the Stirling approximation, would be [cf. equation (50.27)]

$$\ln G = \sum_i (n_i \ln g_i - n_i \ln n_i) + n \ln n. \quad (55.10)$$

However, it has been noted in Section 50j that in order to allow for the indistinguishability of the n elements constituting the system, it is necessary to divide G by $n!$; this is equivalent to the subtraction of $\ln n!$, equal to $n \ln n - n$, from the expression for $\ln G$. If this correction is applied to equation (55.10), the result becomes identical with equation (55.9), as is to be expected. It follows, therefore, that for such conditions that classical statistics may be employed, the quantity S defined by equation (55.6) becomes

$$S = k \ln G = \sum_i k(n_i \ln g_i - n_i \ln n_i + n_i). \quad (55.11)$$

Further, under these same conditions the appropriate form of the distribution law is

$$n_i = \frac{g_i}{e^{\alpha + \beta \epsilon_i}}, \quad (55.12)$$

so that

$$\ln g_i = \ln n_i + (\alpha + \beta \epsilon_i);$$

and hence equation (55.11) can be written as

$$\begin{aligned} S &= \sum_i k n_i (\alpha + \beta \epsilon_i + 1) \\ &= k n \alpha + k \beta E + k n, \end{aligned} \quad (55.13)$$

where E , equal to $\sum n_i \epsilon_i$, is the total energy of the n elements constituting the system.

It should be noted that the constant k used here is that derived from equation (55.6), and has not, so far, been identified with the Boltzmann constant. In order to retain this distinction for the present, it will be supposed that the system under consideration consists of monatomic molecules of an ideal gas; it is then possible to define β in terms of the total energy E by means of equation (48.32), thus

$$\beta = \frac{3n}{2E}. \quad (55.14)$$

If this result is introduced into equation (55.13), it is evident that

$$\begin{aligned} S &= kn\alpha + \frac{3}{2}kn + kn \\ &= kn\alpha + \frac{5}{2}kn. \end{aligned} \quad (55.15)$$

It was seen in Section 51c that the constant B is equal to e^α , and using the result of equation (51.26), but replacing kT by $1/\beta$, it follows that

$$e^\alpha = B = \frac{Q_i}{nh^3} \left(\frac{2\pi m}{\beta} \right)^{3/2} V, \quad (55.16)$$

and since β is equal to $3n/2E$, by equation (55.14),

$$e^\alpha = \frac{Q_i}{nh^3} \left(\frac{4\pi m E}{3n} \right)^{3/2} V, \quad (55.17)$$

where, as before, Q_i is a statistical weight factor for spin, etc. Taking logarithms of equation (55.17), the result is

$$\alpha = \ln \frac{Q_i}{nh^3} \left(\frac{4\pi m E}{3n} \right)^{3/2} V. \quad (55.18)$$

Insertion of this result into equation (55.15), and changing n to N , the Avogadro number, so as to give the value of S for a mole of ideal monatomic gas, it is seen that

$$S = kN \ln \left\{ \frac{Q_i}{Nh^3} \left(\frac{4\pi m E}{3N} \right)^{3/2} V \right\} + \frac{5}{2}kN, \quad (55.19)$$

where V is now the molar volume.

If this expression is differentiated with respect to E , at constant volume, the result is

$$\left(\frac{\partial S}{\partial E} \right)_V = \frac{3kN}{2E}, \quad (55.20)$$

and in view of the definition of S , by equation (55.6), this quantity must represent a temperature. Further, differentiation of equation (55.19) with respect to V , at constant energy, gives

$$\left(\frac{\partial S}{\partial V} \right)_E = \frac{kN}{V}, \quad (55.21)$$

which has the dimensions of energy/volume \times temperature, or pressure/temperature.

If the quantity defined as S by equation (55.6), and which has the properties given by equations (55.20) and (55.21), were really the entropy, then the thermodynamic equations

$$\left(\frac{\partial S}{\partial E} \right)_V = \frac{1}{T} \quad \text{and} \quad \left(\frac{\partial S}{\partial V} \right)_E = \frac{P}{T} \quad (55.22)$$

would hold. For a mole of an ideal monatomic gas, E is equal to $\frac{3}{2}RT$, and P to RT/V ; it then follows from the equations (55.22) that

$$\left(\frac{\partial S}{\partial E}\right)_V = \frac{3R}{2E} \quad (55.23)$$

and

$$\left(\frac{\partial S}{\partial V}\right)_E = \frac{R}{V}. \quad (55.24)$$

Comparison of equation (55.20) with (55.23), and of equation (55.21) with (55.24) shows that if the constant k is identified with the Boltzmann constant, i.e., R/N , then the quantity S as defined by equation (55.6) has the essential properties of thermodynamic entropy. This equation will therefore be used as the quantum statistical definition of entropy; as will be seen shortly, it provides an important approach to thermodynamics through statistics.

55c. Eigenstates and Energy Range.—Before proceeding to a more detailed consideration of thermodynamic functions, reference may be made to the quantity G , the number of eigenstates of the system. As calculated in previous sections, this refers to the number of eigenstates for energy lying within the energy range between E and $E + \delta E$, but the exact magnitude of the range δE has not been specified; all that has been stipulated is that it should be small enough to be treated as an infinitesimal quantity, but it must be large in comparison with the uncertainty ΔE in the evaluation of the energy. Since the entropy as given by equation (55.6) depends on the number of eigenstates of the system, it would seem, therefore, at first sight, that the vagueness in the definition of δE would make the entropy unreliable. It can be shown, however, that because of the enormous magnitude of the quantity G , the error introduced into the entropy on account of the indefiniteness in δE is completely negligible. The simplest way to prove this is to consider some actual figures. The entropies of most gases at standard temperature and pressure are of the order of 10 to 100 cal. per degree, per mole of substance; since the Boltzmann constant k is 1.38×10^{-16} erg per degree, it is readily seen from equation (55.6) that $\ln G$ must be in the vicinity of 10^{25} .

Suppose now that in estimating the number of eigenstates G , the result was in error by the large factor of 10^{100} , because of the indefinite nature of δE ; since $\ln 10^{100}$ is only 230, the error in $\ln G$, which is the important matter, is obviously quite negligible in comparison with the actual value of 10^{25} . It will be apparent that the estimate of G would need to be incorrect by a factor of $10^{10^{25}}$ if the entropy is to be in error by only one part in a thousand. This condition might arise if the energy range δE were taken to be extremely small; it can be shown, however, by means of the uncertainty principle, that δE would then have to be much smaller than the uncertainty ΔE in the evaluation of the energy, and this is not permitted by the restriction on the magnitude of δE given above. Since $\Delta E \Delta t$ is approximately equal to h , by

the Heisenberg principle, the error Δt in the estimate of the time would have to be impossibly large so as to make ΔE small enough for it to be smaller than the δE required to produce an appreciable error in the entropy. The question raised by the indefiniteness in the value of the energy range δE can thus be dismissed, at least as far as the derivation of the entropy from the calculated number of eigenstates is concerned.

55d. Thermodynamic Functions of a Monatomic Gas.—Under such conditions that classical statistics are obeyed by a monatomic gas, which will be under all normal conditions of temperature and pressure, the entropy of one mole of the gas will be given by equation (55.19), viz.,

$$S = kN \ln \left\{ \frac{Q_i}{Nh^3} \left(\frac{4\pi m E}{3N} \right)^{3/2} V \right\} + \frac{5}{2}kN,$$

where k is now to be identified with the Boltzmann constant. Replacing E by $\frac{3}{2}NkT$, it follows that

$$S = kN \ln \left\{ Q_i \frac{(2\pi mkT)^{3/2}}{Nh^3} V \right\} + \frac{5}{2}kN, \quad (55.25)$$

$$= R \ln \left\{ Q_i \frac{(2\pi mkT)^{3/2}}{Nh^3} V \right\} + \frac{5}{2}R, \quad (55.26)$$

which is a form of the Sackur-Tetrode equation for the entropy of one mole of an ideal monatomic gas.² The molar volume V may be replaced by kNT/P , so that an alternative form of equation (55.25), is

$$S = kN \ln \left\{ Q_i \frac{(2\pi mkT)^{3/2}}{h^3} \cdot \frac{kT}{P} \right\} + \frac{5}{2}kN \quad (55.27)$$

$$= R \ln \left\{ Q_i \frac{(2\pi mkT)^{3/2}}{Nh^3} \cdot \frac{RT}{P} \right\} + \frac{5}{2}R. \quad (55.28)$$

The equation for the entropy may be stated in another manner which will be generalized at a later stage. It was seen in Section 52a that a quantity Q_i could be defined by

$$Q_i = \frac{(2\pi mkT)^{3/2}}{h^3} V, \quad (55.29)$$

where V is here the molar volume; further, the product of Q_i and the statistical weight factor Q_i was represented by Q , in equation (52.5), so that

$$Q = Q_i \frac{(2\pi mkT)^{3/2}}{h^3} V. \quad (55.30)$$

² Sackur, *Ann. Physik*, 40, 67 (1913); Tetrode, *ibid.*, 38, 434 (1912); 39, 255 (1913); Stern, *Physikal. Z.*, 14, 629 (1913).

Upon taking logarithms, viz.,

$$\ln Q = \ln \left\{ Q_i \frac{(2\pi mkT)^{3/2}}{h^3} V \right\}, \quad (55.31)$$

and differentiating with respect to temperature, at constant volume, it is found that

$$T \left(\frac{\partial \ln Q}{\partial T} \right)_V = \frac{3}{2}. \quad (55.32)$$

Comparison of equations (55.31) and (55.32) with equation (55.25), shows that the latter may be written as

$$S = kN \ln \frac{Q}{N} + kNT \left(\frac{\partial \ln Q}{\partial T} \right)_V + kN,$$

and, making use of the Stirling approximation, viz., $\ln N! = N \ln N - N$, this becomes

$$S = k \ln \frac{Q^N}{N!} + kNT \left(\frac{\partial \ln Q}{\partial T} \right)_V. \quad (55.33)$$

Another analogous expression for S is obtained by replacing V in equation (55.31) by kNT/P , and differentiating with respect to temperature, at constant pressure; the result is

$$T \left(\frac{\partial \ln Q}{\partial T} \right)_P = \frac{5}{2}. \quad (55.34)$$

Comparison with equation (55.25), then leads to the form

$$S = kN \left\{ \ln \frac{Q}{N} + T \left(\frac{\partial \ln Q}{\partial T} \right)_P \right\}. \quad (55.35)$$

It should be noted that in the foregoing derivations it has been tacitly assumed that Q_i is independent of temperature; this is strictly true for atoms, or monatomic molecules, provided they are all, or virtually all, in their electronic ground states.

The Gibbs free energy F can be derived from the equation for the entropy by making use of the familiar thermodynamic relationship

$$F = E + PV - TS. \quad (55.36)$$

For an ideal monatomic gas,

$$E = \frac{3}{2}PV,$$

and since $PV = RT$ for one mole, it follows that

$$F = \frac{5}{2}RT - TS. \quad (55.37)$$

Utilizing the value of S given by equation (55.26) or (55.28), it is seen that

$$F = -RT \ln \left\{ \frac{Q_i}{N} \cdot \frac{(2\pi mkT)^{3/2}}{h^3} \cdot \frac{RT}{P} \right\} \quad (55.38)$$

$$= -RT \ln \left\{ \frac{Q_i}{N} \cdot \frac{(2\pi mkT)^{3/2}}{h^3} V \right\} \quad (55.39)$$

$$= -kNT \ln \frac{Q}{N}. \quad (55.40)$$

An analogous expression can be obtained for the Helmholtz free energy (maximum work function) represented by A ; this is given by

$$\begin{aligned} A &= F - PV \\ &= F - RT = F - kNT, \end{aligned} \quad (55.41)$$

for one mole of an ideal gas. Making use of equation (55.40), the maximum work function for the one mole of monatomic gas is

$$\begin{aligned} A &= -kNT \ln \frac{Q}{N} - kNT \\ &= -kT \ln Q^N + kT(N \ln N - N) \\ &= -kT \ln \frac{Q^N}{N!}, \end{aligned} \quad (55.42)$$

after introducing the Stirling approximation for $\ln N!$.

55e. Calculation of the Thermionic Current.—It was mentioned in Section 53d that it is possible to derive the Richardson equation (53.46) for the thermionic current by considering the rate at which electrons from the vapor phase return to the metal at equilibrium; this calculation can now be made with the aid of equation (55.40). The average energy required to take an electron from the interior of the metal and bring it, in a state of rest, outside the metal is equal to the thermionic work function χ . Since the transfer process involves no mechanical work against an external pressure, the quantity χ may be identified with the free energy change accompanying the electron transfer. Regarding the free energy of the electron at rest outside the metal as zero, the value for an electron inside the metal will be equal to $-\chi$. The thermodynamic condition for equilibrium is that the free energy per electron, at constant temperature and pressure, must be the same inside the metal as it is in the vapor phase, and hence the latter must also have the value $-\chi$. Since the density of electrons in the vapor is very small, the system will approach classical behavior, and hence the free energy per electron in the vapor will be obtained on dividing equation (55.40)

by the Avogadro number; consequently,

$$\begin{aligned} -\chi &= \frac{F}{N} = -kT \ln \frac{Q}{N} \\ &= -kT \ln \left\{ \frac{Q_i}{N} \cdot \frac{(2\pi mkT)^{3/2}}{h^3} \cdot \frac{RT}{P} \right\}. \end{aligned} \quad (55.43)$$

Noting that for electrons Q_i is equal to 2, because of the spin degeneracy, and solving equation (55.43) for P , the electron gas pressure, it is found that

$$P = \frac{2(2\pi mkT)^{3/2}}{h^3} kT e^{-\chi/kT}. \quad (55.44)$$

According to kinetic theory the pressure of a gas is related to the number of particles Z striking a surface of unit area in unit time by the expression

$$Z = P(2\pi mkT)^{-1/2},$$

and if the value of P given by equation (55.44) is introduced, the result is

$$Z = \frac{4\pi mk^2 T^2}{h^3} e^{-\chi/kT}.$$

This is seen to be identical with equation (53.45), and hence if the value of Z as given here is multiplied by the electronic charge, there will be obtained the Richardson equation for the thermionic current in exactly the same form as in equation (53.46).

THE PARTITION FUNCTION³

56a. Generalized Equations for Thermodynamic Functions: The Partition Function.—Up to the present the concepts of statistical mechanics have been employed to study systems made up of point particles, such as monatomic molecules and electrons, so that the energy has been restricted to that which is purely translational in character. It is important to emphasize, however, that there is nothing in the derivation of the general equations, giving the values of G for the number of eigenstates of a system, that restricts their application to energy of a particular type; exactly the same conclusion holds for the distribution laws derived from the expressions for the number of eigenstates. It follows, therefore, that equation (55.10) for the value of $\ln G$, and equation (55.11) for the entropy, equal to $k \ln G$, are applicable to the total for the molecule, including translational, vibrational, rotational, etc., contributions. It is true that the value of k has been identified with the Boltzmann constant for a monatomic gas, but the arguments could be ex-

³ Giauque, *J. Am. Chem. Soc.*, **52**, 4808 (1930); Rodebush, *Chem. Rev.*, **9**, 319 (1931); Kassel, *ibid.*, **18**, 277 (1936); Wilson, *ibid.*, **27**, 17 (1940); Glasstone, *Ann. Rep. Chem. Soc.*, **32**, 66 (1935); Zeise, *Z. Elektrochem.*, **39**, 758, 895 (1933); **40**, 662, 885 (1934); **48**, 476 (1942); Thompson, *Ann. Rep. Chem. Soc.*, **38**, 54 (1941).

tended so as to be applicable to any system of weakly interacting, i.e., ideal, molecules. Further, the classical distribution equation gives the number of molecules n_i having a *total* energy in the range ϵ_i to $\epsilon_i + \delta\epsilon_i$ viz.,

$$n_i = \frac{g_i}{e^{\alpha + \epsilon_i/kT}} = \frac{g_i}{B} e^{-\epsilon_i/kT}, \quad (56.1)$$

where, as before, B is used in place of e^α . It follows, therefore, that

$$e^\alpha = B = \frac{g_i}{n_i} e^{-\epsilon_i/kT}. \quad (56.2)$$

The sum of all the values of n_i is equal to the total number of molecules n , so that by equation (56.1)

$$\begin{aligned} n &= \sum_i n_i = \frac{1}{B} \sum_i g_i e^{-\epsilon_i/kT} \\ \therefore B &= \frac{1}{n} \sum_i g_i e^{-\epsilon_i/kT}. \end{aligned} \quad (56.3)$$

The quantity $\sum g_i e^{-\epsilon_i/kT}$, which represents the sum of all the $g_i e^{-\epsilon_i/kT}$ terms for every quantum level of energy of a single molecule, is generally referred to as the *partition function* of the given molecule, and is represented by the symbol Q .⁴

It is therefore possible to write the definition

$$Q = \sum_i g_i e^{-\epsilon_i/kT}, \quad (56.4)$$

and hence equation (56.2) becomes

$$e^\alpha = B = \frac{Q}{n}. \quad (56.5)$$

It will be observed that this result is identical with the classical value of B derived in previous sections; this is, in fact, why the symbol Q was used in the earlier work to represent certain expressions. The fundamental definition for Q is given by equation (56.4), but it will be seen later that in the special case of a monatomic gas this becomes identical with the earlier definitions, such as are represented by equations (52.4) and (52.5).

The use of the partition function, in its most general form, permits the ready derivation of expressions for the various thermodynamic properties that are applicable to molecules of all types; only one condition need be made, namely, that classical statistics are applicable, and this will be the case at all reasonable temperatures and pressures for a system of weakly interacting particles. This means, of course, that the system must consist

⁴ The partition function was originally called the *Zustandssumme* by Planck, and this was translated as "sum over states" or "state sum," but these terms are now rarely used.

of an ideal, or virtually ideal, gas. The general method will now be applied to a number of important thermodynamic functions.

56b. Entropy and Free Energy.—As seen in Section 55b, the number of eigenstates of any system which may be treated as behaving classically is given by equation (55.9), viz.,

$$\ln G = \sum_i (n_i \ln g_i - n_i \ln n_i + n_i),$$

and if the fundamental postulate for the entropy, namely

$$S = k \ln G$$

is introduced, it follows, as before, that

$$S = \sum_i k(n_i \ln g_i - n_i \ln n_i + n_i).$$

Further, by using the classical distribution law equation

$$n_i = \frac{g_i}{e^{\alpha + \epsilon_i/kT}},$$

and the expression

$$E = \sum n_i \epsilon_i,$$

for the total energy, it is found that [cf. equation (55.13)],

$$S = \frac{E}{T} + kn\alpha + kn,$$

where k is now identified with the Boltzmann constant. For one mole, n is replaced by the Avogadro number N ; hence,

$$\begin{aligned} S &= \frac{E}{T} + kN\alpha + kN \\ &= \frac{E}{T} + R\alpha + R. \end{aligned} \tag{56.6}$$

For a system of N molecules, it follows from equation (56.5) that

$$e^{\alpha} = \frac{Q}{N},$$

where Q is still the partition function for a single molecule, so that

$$\alpha = \ln \frac{Q}{N}, \tag{56.7}$$

and hence equation (56.6) becomes

$$S = \frac{E}{T} + R \ln \frac{Q}{N} + R. \tag{56.8}$$

Using the thermodynamic definition $F = E + PV - TS$, or its equivalent for an ideal gas,

$$F = E + RT - TS,$$

it follows from equation (56.8) that

$$F = -RT \ln \frac{Q}{N}. \quad (56.9)$$

Combination of this result with the thermodynamic equation

$$\left(\frac{\partial F}{\partial T} \right)_P = -S$$

permits equation (56.8) to be written in the form

$$S = R \left\{ \ln \frac{Q}{N} + T \left(\frac{\partial \ln Q}{\partial T} \right)_P \right\}. \quad (56.10)$$

Further, since the maximum work function \mathcal{A} is equal to $F - RT$ for 1 mole of an ideal gas, it follows from equation (56.9) that

$$\mathcal{A} = -RT \ln \frac{Q}{N} - RT,$$

and use of the Stirling approximation for $\ln N!$, as in Section 55d, gives

$$\mathcal{A} = -kT \ln \frac{Q^N}{N!}. \quad (56.11)$$

The use of the thermodynamic relationship

$$\left(\frac{\partial \mathcal{A}}{\partial T} \right)_V = -S,$$

now provides another form of equation (56.10), namely

$$S = k \ln \frac{Q^N}{N!} + RT \left(\frac{\partial \ln Q}{\partial T} \right)_V. \quad (56.12)$$

It will be observed that equations (56.9), (56.10), (56.11) and (56.12), are identical with the equations (55.40), (55.35), (55.42) and (55.33), respectively; the reason for this identity, as indicated above, is that the quantity Q , defined by equation (52.4), viz.,

$$Q = \frac{(2\pi mkT)^{3/2}}{h^3} V$$

or, by its equivalent,

$$Q_t = \frac{(2\pi mkT)^{3/2}}{h^3} \cdot \frac{RT}{P},$$

is, in fact, the partition function for translational energy, as will be seen shortly. If this is multiplied by the statistical weight factor Q_i , which allows for nuclear spin, etc., the resulting quantity $Q_t Q_i$, which was represented by Q , gives the complete partition function for the monatomic molecule. This accounts for the identity of the two sets of equations. For monatomic molecules that are not all in their lowest electronic (ground) state, and also for polyatomic molecules, Q_i must, however, include factors other than that due to nuclear spin; this matter will be considered later.

56c. Energy and Heat Capacity.—The total energy E is represented thermodynamically by

$$E = A + TS,$$

and utilizing equations (56.11) and (56.12) for A and S , respectively, the result is

$$E = RT^2 \left(\frac{\partial \ln Q}{\partial T} \right)_v. \quad (56.13)$$

This equation may be written in a variety of other forms, such as

$$E = \frac{RT^2}{Q} \left(\frac{\partial Q}{\partial T} \right)_v \quad (56.14)$$

$$= -R \left\{ \frac{\partial \ln Q}{\partial (1/T)} \right\}_v \quad (56.15)$$

$$= -\frac{R}{Q} \left\{ \frac{\partial Q}{\partial (1/T)} \right\}_v. \quad (56.16)$$

The quantity Q' may be defined as

$$Q' = \left\{ \frac{\partial Q}{\partial (1/T)} \right\}_v = -T^2 \left(\frac{\partial Q}{\partial T} \right)_v, \quad (56.17)$$

and utilizing the definition of Q given by equation (56.4), it follows that

$$Q' = - \sum_i \frac{\epsilon_i}{k} g_i e^{-\epsilon_i/kT}. \quad (56.18)$$

Hence equation (55.16) may be written as

$$E = -\frac{R}{Q} Q', \quad (56.19)$$

where Q' could be evaluated by means of equation (56.18).

The heat capacity at constant volume may be obtained by differentiating the expression for E with respect to T , at constant volume; the results are

$$C_V = \frac{\partial}{\partial T} \left\{ RT^2 \left(\frac{\partial \ln Q}{\partial T} \right) \right\}_V \quad (56.20)$$

$$= -R \frac{\partial}{\partial T} \left\{ \frac{\partial \ln Q}{\partial (1/T)} \right\}_V \quad (56.21)$$

$$= \frac{R}{T^2} \left\{ \frac{\partial^2 \ln Q}{\partial (1/T)^2} \right\}_V. \quad (56.22)$$

If in addition to Q' , as given by equations (56.17) and (56.18), a further quantity Q'' is defined by

$$Q'' = \left\{ \frac{\partial^2 Q}{\partial (1/T)^2} \right\}_V \quad (56.23)$$

$$= \sum_i \left(\frac{\epsilon_i}{k} \right)^2 g_i e^{-\epsilon_i/kT}, \quad (56.24)$$

equation (56.22) can be written as

$$C_V = \frac{R}{T^2} \left\{ \frac{Q''}{Q} - \left(\frac{Q'}{Q} \right)^2 \right\}. \quad (56.25)$$

The heat content H is equal to $E + PV$, and so for one mole of an ideal gas, it follows that

$$\begin{aligned} H &= E + RT \\ &= F + TS, \end{aligned}$$

and hence from equations (56.9) and (56.10),

$$H = RT^2 \left(\frac{\partial \ln Q}{\partial T} \right)_P. \quad (56.26)$$

Differentiation with respect to temperature, at constant pressure, gives

$$C_P = \frac{\partial}{\partial T} \left\{ RT^2 \left(\frac{\partial \ln Q}{\partial T} \right) \right\}_P. \quad (56.27)$$

The expressions for H and C_P are seen to be identical in form with those for E and C_V , respectively; the only difference is that in the former case the differentiation is always at constant pressure, while for the latter it is at constant volume. If this is borne in mind, one set of equations is adequate to cover all the conditions.

56d. Alternative Derivation of Thermodynamic Equations.—There is another approach to the question of the relationship between the partition

function and the various thermodynamic functions that is of interest. By combining equations (56.1) and (56.5), it is seen that for a system of N molecules

$$n_i = \frac{N}{Q} g_i e^{-\epsilon_i/kT}, \quad (56.28)$$

and since the total energy E per mole is equal to $\sum n_i \epsilon_i$ for all states of the system, it follows that

$$\begin{aligned} E &= \frac{N}{Q} \sum_i \epsilon_i g_i e^{-\epsilon_i/kT} \\ &= \frac{kN}{Q} \sum_i \frac{\epsilon_i}{k} g_i e^{-\epsilon_i/kT}. \end{aligned} \quad (56.29)$$

As seen from equation (56.18), the summation in equation (56.29) is equal to $-Q'$ and hence

$$E = -\frac{R}{Q} Q', \quad (56.30)$$

as given by equation (56.19). The alternative forms, equations (56.14), (56.15) and (56.16), then follow immediately. From these, the various expressions for C_V may then be derived by differentiation with respect to temperature, as shown above.

The evaluation of the entropy may now be made by utilizing the thermodynamic equation

$$dS = \frac{C_V}{T} dT,$$

so that

$$S - S_0 = \int_0^T \frac{C_V}{T} dT,$$

where S is the molar entropy of the gas at the temperature T , and S_0 is the hypothetical value at the absolute zero. Introducing the value of C_V given by the equation

$$C_V = \frac{\partial}{\partial T} \left\{ RT^2 \left(\frac{\partial \ln Q}{\partial T} \right) \right\}_V,$$

which is equivalent to equation (56.30), it follows that

$$\begin{aligned} S - S_0 &= \int_0^T \frac{1}{T} \cdot \frac{\partial}{\partial T} \left\{ RT^2 \left(\frac{\partial \ln Q}{\partial T} \right) \right\}_V dT \\ &= \frac{RT^2}{T} \left(\frac{\partial \ln Q}{\partial T} \right)_V + \int_0^T \frac{RT^2}{T^2} \left(\frac{\partial \ln Q}{\partial T} \right)_V dT \\ &= RT \left(\frac{\partial \ln Q}{\partial T} \right)_V + R \ln Q - R \ln Q_0, \end{aligned} \quad (56.31)$$

where Q_0 is the hypothetical partition function of one molecule of the gas at the absolute zero.

The next step in the calculation is the elimination of S_0 , and it is at this point that the postulated relationship between the entropy and the number of eigenstates, viz.,

$$S = k \ln G$$

is introduced. If g_i is assumed to be greater than n_i , so that classical statistics are applicable, then by equation (55.9),

$$\ln G = \sum_i (n_i \ln g_i - n_i \ln n_i + n_i), \quad (56.32)$$

but at the absolute zero all the N molecules will presumably be in the same, i.e., the lowest, energy state; hence, using the subscript zero to indicate this condition, equation (56.32) becomes

$$\begin{aligned} \ln G_0 &= N \ln g_0 - N \ln N + N \\ &= N \ln g_0 - \ln N! \end{aligned}$$

$$\therefore S_0 = k \ln G_0 = R \ln g_0 - k \ln N! \quad (56.33)$$

It should be noted that this entropy is the value that an ideal gas would have at the absolute zero if it remained in the ideal gaseous state at this temperature; it must be regarded, in effect, as an extrapolated, rather than as a real quantity.

If the energy of any quantum state is reckoned from the value at the absolute zero of temperature as the zero of energy, the term $e^{-\epsilon/kT}$ is unity; hence the partition function Q_0 at the absolute zero becomes equal to g_0 , there being but one energy level. Consequently g_0 in equation (56.33) may be replaced by Q_0 , giving

$$S_0 = R \ln Q_0 - k \ln N! \quad (56.34)$$

Introducing this result into equation (56.31), it is found that

$$\begin{aligned} S &= RT \left(\frac{\partial \ln Q}{\partial T} \right)_v + R \ln Q - k \ln N! \\ &= RT \left(\frac{\partial \ln Q}{\partial T} \right)_v + k \ln \frac{Q^N}{N!}, \end{aligned}$$

which is identical with equation (56.12).

Since expressions for E and S have been derived, it is evidently a simple matter to deduce the same equations as before for the other thermodynamic functions, viz., H , F and A .

56e. Effect of Zero Energy Level.—Since the partition function involves the summation of a number of exponential terms containing the energies of all possible levels in the molecule, it is necessary to consider the level that is to be taken as the energy zero. For gases, it is the general practice to

take the zero-point level of each molecule, i.e., the level for which the translational, vibrational and rotational quantum numbers are all zero, as the energy zero. It is of interest, however, to see what would be the effect of changing the energy zero to any other arbitrary level. Let ϵ_i be the energy of the i th level, the energy being reckoned from the zero-point level of the molecule; the partition function is then given in the usual manner by

$$Q = \sum g_i e^{-\epsilon_i/kT}.$$

Suppose now that the energy zero is changed by an amount ϵ_0 ; the energy value of each level is then changed by an equal amount, so that the new partition function, designated Q_{E_0} , will be given by

$$\begin{aligned} Q_{E_0} &= \sum g_i e^{-(\epsilon_0 + \epsilon_i)/kT} \\ &= e^{-\epsilon_0/kT} \sum g_i e^{-\epsilon_i/kT} \\ &= e^{-\epsilon_0/kT} Q. \end{aligned} \quad (56.35)$$

The new partition function is thus equal to the original value multiplied by $e^{-\epsilon_0/kT}$, where ϵ_0 is the change in the energy zero per molecule. If E_0 is the energy change per mole, which is equal to $N\epsilon_0$, where N is the Avogadro number, then equation (56.35) may be written as

$$Q_{E_0} = e^{-E_0/RT} Q. \quad (56.36)$$

Upon taking logarithms of equation (56.36), it is seen that

$$\ln Q_{E_0} = \ln Q - \frac{E_0}{RT}, \quad (56.37)$$

and hence,

$$\frac{\partial \ln Q_{E_0}}{\partial T} = \frac{\partial \ln Q}{\partial T} + \frac{E_0}{RT^2}. \quad (56.38)$$

From these equations, and bearing in mind the expressions for the various energy functions E , H , F and A , it can readily be seen that the values of these functions, based on the new energy zero, will be E_0 per mole greater than those based on the original zero level. This is, of course, exactly what is to be expected. On the other hand, the entropy and heat capacity are found to be independent of the arbitrarily chosen energy zero.

DETERMINATION OF PARTITION FUNCTIONS

57a. Separation of Partition Functions.—For the purpose of calculating partition functions, it is convenient to separate the energy of a molecule into at least two independent parts; one part, the translational energy, is determined solely by the coordinates and momenta of the center of mass of the molecule, while the other part depends on all other (internal) degrees of freedom. If ϵ_t represents the translational energy of a molecule in any

given state, and ϵ_i is the whole of the residual energy, including rotational, vibrational, electronic and nuclear forms, the total energy ϵ is then given by

$$\epsilon = \epsilon_t + \epsilon_i,$$

and hence

$$e^{-\epsilon/kT} = e^{-\epsilon_t/kT} e^{-\epsilon_i/kT}. \quad (57.1)$$

The complete partition function for the molecule may now be separated into two parts; the number of eigenfunctions (statistical weight) g of a system will be equal to the product of the eigenfunctions for the different forms of energy; hence, in view of equation (57.1), the partition function may be written as

$$Q = \sum_i g_i e^{-\epsilon_i/kT} \sum_j g_j e^{-\epsilon_j/kT}, \quad (57.2)$$

where the subscript i refers here to all the internal energy states. The translational energy states are apparently nondegenerate, so that the statistical weight g_i is unity; it is then possible to write

$$Q = Q_t Q_i,$$

in agreement with the definition used earlier, where

$$Q_t = \sum_i e^{-\epsilon_i/kT} \quad \text{and} \quad Q_i = \sum_j g_j e^{-\epsilon_j/kT}. \quad (57.3)$$

The fact that the complete partition function may be written as the product of the partition functions for external (translational) and internal degrees of freedom now permits a partial simplification of the problem of evaluating the quantity Q for a given molecular species. A further separation of Q_i will be considered shortly, but in the meantime the derivation of the translation partition function Q_t will be described.

57b. The Translational Partition Function.—The translational energy of a molecule can be treated as involving three independent components in directions at right angles; in any one direction, the quantum mechanical expression for the translational energy per molecule $\epsilon_{t(1)}$ is given by [cf. equation (51.5)]

$$\epsilon_{t(1)} = \frac{n^2 h^2}{8ml^2},$$

where n is the appropriate quantum number. The partition function for one degree of translational freedom is consequently given, according to equation (57.3), by

$$\begin{aligned} Q_{t(1)} &= \sum_i e^{-\epsilon_{t(1)}/kT} \\ &= \sum_{n=0}^{\infty} e^{-n^2 h^2 / 8ml^2 kT}, \end{aligned}$$

the summation being carried over all values of the quantum number n from zero to infinity. Since the translational levels are very closely spaced, that is to say, the quanta are extremely small, the summation may be replaced by integration; hence

$$Q_{t(1)} = \int_0^\infty e^{-n^2 h^2 / 8ml^2 kT} dn.$$

Replacing the constant factor $h^2/8ml^2kT$ by the symbol λ , the expression for the translational partition function in one degree of freedom becomes

$$\begin{aligned} Q_{t(1)} &= \int_0^\infty e^{-n^2 \lambda} = \frac{1}{2} \left(\frac{\pi}{\lambda} \right)^{1/2} \\ &= \frac{(2\pi mkT)^{1/2}}{h} l. \end{aligned} \quad (57.4)$$

The contributions for the three translational degrees of freedom are the same, and so the complete partition function Q_t for a single molecule is obtained by multiplication of the three identical expressions; thus

$$Q_t = \frac{(2\pi mkT)^{3/2}}{h^3} V \quad (57.5)$$

$$= \frac{(2\pi mkT)^{3/2}}{h^3} \cdot \frac{RT}{P}, \quad (57.6)$$

where l has been replaced by the molar volume V , or by RT/P . It will be observed that these equations for the partition function Q_t are identical with that assumed previously, e.g., equation (55.29), in defining Q_t .

Attention should be drawn to the fact that equation (57.5) is the general expression for the translational partition function of a *single molecule* moving in a vessel of volume V , irrespective of the magnitude of the latter. Provided the interaction between them is small, as in an ideal gas, the presence of other molecules in the volume is immaterial. When using partition functions to calculate thermodynamic quantities for 1 mole of (ideal) gas, as in the present chapter, V becomes the molar volume, and then equation (57.6) is also applicable. The partition function is, nevertheless, still that for a single molecule; the question of the combined partition function for all the molecules in a mole of gas will be considered in Chapter IX.

It is of interest at this point to consider the equivalent of the partition function in classical statistical mechanics; this is often useful, for under correspondence principle limits it gives the same results as does the quantum statistical treatment. Utilizing the definition of g given by equation (51.2), the classical expression for the partition function becomes

$$Q = \frac{1}{h^f} \int \cdots \int e^{-\epsilon/kT} dq_1 \cdots dp_f. \quad (57.7)$$

The energy ϵ should be expressed in Hamiltonian form, i.e., as a function $H(p, q)$ of the coordinates and the momenta, so that equation (57.7) is often written in the form

$$Q = \frac{1}{h^f} \int \cdots \int e^{-H(p, q)/kT} dq_1 \cdots dp_f. \quad (57.8)$$

These equations for the partition function are satisfactory under such conditions that the quantum states of the appropriate energy are very close together; in general, the difference of energy between two successive states should be small in comparison with kT if the classical equations are to be adequate. This condition is particularly applicable to translational energy, and so it is possible to write, for a single molecule,

$$\epsilon_t = H(p, q) = \frac{1}{2m} (p_x^2 + p_y^2 + p_z^2),$$

and hence the translational partition function is

$$Q_t = \frac{1}{h^3} \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} e^{-(p_x^2 + p_y^2 + p_z^2)/2mkT} dx dy dz dp_x dp_y dp_z.$$

Integration over the coordinates x, y, z gives the volume V of the containing vessel; hence

$$Q_t = \frac{V}{h^3} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-(p_x^2 + p_y^2 + p_z^2)/2mkT} dp_x dp_y dp_z,$$

and comparison with the integrals in Section 48b shows that

$$Q_t = \frac{(2\pi mkT)^{3/2}}{h^3} V,$$

as found above.

57c. Translational Thermodynamic Functions.—The partition functions just derived may be used to illustrate the calculation of thermodynamic functions corresponding to translational energy. The molar translational entropy S_t , for example, may be derived from equation (56.12), which takes the form

$$\begin{aligned} S_t &= k \ln \frac{Q_t^N}{N!} + RT \left(\frac{\partial \ln Q_t}{\partial T} \right)_V \\ &= R \ln \left\{ \frac{(2\pi mkT)^{3/2}}{h^3} V \right\} - k \ln N! + \frac{3}{2}R. \end{aligned} \quad (57.9)$$

Since $\ln N!$ is equal to $N \ln N - N$ by the Stirling approximation,

$$\begin{aligned} k \ln N! &= kN \ln N - kN \\ &= R \ln N - R, \end{aligned}$$

and if this is inserted in equation (57.9) the result is

$$S_t = R \ln \left\{ \frac{(2\pi mkT)^{3/2}}{Nh^3} V \right\} + \frac{5}{2}R, \quad (57.10)$$

which is the original form of the Sackur-Tetrode equation. It gives the translational entropy of one mole of any ideal gas, or the total entropy, apart from the nuclear spin contribution, of a monatomic ideal gas [cf. equation (55.26)]. The molar volume V may be replaced by kNT/P , so that equation (57.10) becomes

$$S_t = R \ln \left\{ \frac{(2\pi mkT)^{3/2}}{h^3} \cdot \frac{kT}{P} \right\} + \frac{5}{2}R. \quad (57.11)$$

If the universal constants R , π , k , h and N are separated from m , T and P , which are characteristic properties of the gas, it is seen that

$$S_t = R \left\{ \frac{3}{2} \ln M + \frac{5}{2} \ln T - \ln P + \ln \left(\frac{2\pi k}{h^2 N} \right)^{3/2} k + \frac{5}{2} \right\}.$$

Inserting the values of the constants, and converting the units so that the pressure is in atmospheres, it is found that

$$S_t = 4.576 \left(\frac{3}{2} \log M + \frac{5}{2} \log T - \log P - 0.5053 \right) \quad (57.12)$$

in calories per degree per mole.

The total translational energy E_t is given by equation (56.13) in the form

$$E_t = RT^2 \left(\frac{\partial \ln Q_t}{\partial T} \right)_V, \quad (57.13)$$

and using the value for Q_t derived above, it follows that

$$\begin{aligned} E_t &= RT^2 \left\{ \frac{\partial}{\partial T} \ln \frac{(2\pi mkT)^{3/2}}{h^3} V \right\}_V \\ &= \frac{3}{2}RT, \end{aligned} \quad (57.14)$$

in agreement with expectation. This is identical with the total energy for an ideal monatomic gas, since the nuclear spin statistical weight is independent of temperature and makes no contribution to the energy. The heat capacity at constant volume is, of course, equal to $\frac{3}{2}R$.

The pressure of a gas, which is entirely due to the translational motion, can also be derived from the partition function by using the thermodynamic relationship

$$P = - \left(\frac{\partial A}{\partial V} \right)_T$$

in conjunction with equation (56.10) for A ; the result is

$$P = RT \left(\frac{\partial \ln Q}{\partial V} \right)_T. \quad (57.15)$$

For an ideal gas, the only portion of the partition function that is dependent on the volume is the translational contribution; hence Q may be replaced by Q_t so that

$$\begin{aligned} P &= RT \left\{ \frac{\partial}{\partial V} \ln \frac{(2\pi mkT)^{3/2}}{h^3} V \right\}_T \\ &= \frac{RT}{V}, \end{aligned} \quad (57.16)$$

as required for one mole of an ideal gas.

58a. Atoms and Monatomic Molecules.—For a system consisting of atomic particles the contribution of the internal quantum states to the partition function is restricted to the nuclear spin and electronic angular momentum factors. Single particles have no vibrational or rotational energy, at least none that affects the heat capacity or entropy, and so the internal partition function Q_i is the product of the two factors just mentioned; thus,

$$Q_i = Q_n Q_e, \quad (58.1)$$

where Q_n may be called the nuclear spin partition function, and Q_e is the electronic partition function.

If i is the number of units of spin momentum of the atomic nucleus, there are $2i + 1$ possible orientations, of almost equal energy, that may be taken by the nucleus in a perturbing field (cf. Section 31e). Since the differences between the energies of the nucleus in the various orientations are negligible, the situation is equivalent to a nuclear spin degeneracy equal to $2i + 1$. The nuclear energy may be taken as that corresponding to the atom in its lowest state; hence the expression for the partition function becomes

$$\begin{aligned} Q_n &= \sum g e^{-\epsilon/kT} = (2i + 1) e^{0/kT} \\ &= 2i + 1. \end{aligned} \quad (58.2)$$

The nuclear spin contribution of an atom or a monatomic molecule to the complete partition function is thus a factor of $2i + 1$. For example, the nuclear spin of the hydrogen atom is $\frac{1}{2}$ unit, and consequently the spin factor for this atom is $(2 \times \frac{1}{2}) + 1 = 2$.

The total electronic angular momentum of an atom is determined by the quantum number j , which has only positive values given by $l \pm s$, where l and s have been defined in Section 1. For every j value there are $2j + 1$ different possible orientations in a magnetic field; these orientations represent states of the atom with almost identical energies. The degeneracy of each electronic state is thus $2j + 1$ where j is the appropriate value of

the resultant quantum number; the electronic contribution to the partition function is then given by

$$Q_e = \sum (2j + 1)e^{-\epsilon/kT}, \quad (58.3)$$

the summation being carried over all the electronic states of the atom. For the lowest electronic state, i.e., the ground state, ϵ is zero, and the value of $(2j + 1)e^{-\epsilon/kT}$ for this state is just $2j + 1$. If the energy of the next highest electronic state is considerably greater than that of the ground state, the corresponding $e^{-\epsilon/kT}$ factor is so small that it may be neglected. As a very rough rule, it may be stated that if $h\nu/k$ is greater than $5T$, where ν cm.⁻¹ is the energy of the electronic level above the ground state, expressed in terms of wave numbers, then the contribution of that particular level to the partition function may be neglected, since e^{-5} is equal to 0.0067. For the ground state of atomic hydrogen, for example, the term is $^2S_{1/2}$, so that j is $\frac{1}{2}$, and $2j + 1$ is thus equal to 2. For the first excited states, $h\nu/k$ is equal to 1.18×10^6 , and so a temperature of several thousand degrees would be necessary before this level made any detectable contribution to the partition function. The value of Q_e for atomic hydrogen at all reasonable temperatures is thus 2. As seen above, the nuclear spin contribution is also 2, and so the total partition function for the internal quantum states of atomic hydrogen is given by

$$Q_i = Q_n Q_e = 4.$$

The ground state of the chlorine atom is a $^3P_{3/2}$ term so that j is $\frac{3}{2}$, and the degeneracy $2j + 1$ is 4. The frequency separation of the next highest level, $^3P_{1/2}$, from the lowest state is 881 cm.⁻¹, so that $h\nu/k$ is 1268; this level will thus begin to contribute appreciably to the partition function at temperatures of about 250° K and higher. Since j for the higher electronic state is $\frac{1}{2}$, the degeneracy is 2, and hence the electronic partition function for atomic chlorine is

$$Q_e = 4 + 2e^{-881hc/kT},$$

the energy of higher levels being so large that their contribution can be neglected. The nuclear spin i of the chlorine atom is $\frac{5}{2}$ units, and so Q_n , equal to $2i + 1$, is 6; it follows, therefore, that for atomic chlorine

$$Q_i = 6(4 + 2e^{-881hc/kT}).$$

A slightly more complicated case is presented by atomic oxygen; the ground term is an inverted triplet 3P state, the j values being 2, 1 and 0; the frequency separations of the two higher levels are 157.4 cm.⁻¹ and 226.1 cm.⁻¹, respectively, above the lowest level. Since the nuclear spin of the oxygen atom is zero, Q_n is equal to unity; hence

$$\begin{aligned} Q_i &= (2j_0 + 1)e^{-\epsilon_0/kT} + (2j_1 + 1)e^{-\epsilon_1/kT} + (2j_2 + 1)e^{-\epsilon_2/kT} \\ &= 5 + 3e^{-157.4hc/kT} + e^{-226.1hc/kT}. \end{aligned}$$

At very high temperatures the contributions of excited states must be included.

The complete partition function of an atom or monatomic molecule is obtained by multiplying the value of Q_i , calculated as just described, by Q_e , given by equation (57.5) or (57.6); the resulting expression for Q may be inserted in the equations for the various thermodynamic properties. It should be noted that the Sackur-Tetrode equation for the entropy of a monatomic gas, e.g., equation (55.26) or (55.28), is strictly applicable only if Q_i is a constant, independent of temperature. This will, of course, not be the case if Q_i includes terms for excited electronic states, as is obvious from the expressions for the internal partition functions of atomic chlorine and oxygen given above. In other words, the Sackur-Tetrode equation in its simple form is applicable, strictly, to the ground state only of an ideal atomic species, even if the correct value of Q_i is employed. The general expression for the entropy, e.g., equation (56.10) can, however, always be used, and from it a modified Sackur-Tetrode equation can be obtained if desired; this will include a term involving $\partial \ln Q_i / \partial T$, which is significant only if higher electronic levels make an appreciable contribution to the partition function.

It may be of interest in this connection to observe that the translational energy of $\frac{3}{2}RT$ per mole of ideal gas, as given by equation (57.14), will also represent the total energy of an ideal monatomic species in its ground state. If there are excited electronic states of relatively low energy, these will make a contribution to $\ln Q_i$ that is temperature dependent, and hence will affect the total energy value. The *translational* part of the energy, however, is still $\frac{3}{2}RT$ per mole. Similar considerations apply, of course, to the heat capacity. On the other hand, the pressure as expressed by equation (57.16) remains unaffected, since the expression for P involves the derivative of $\ln Q$ with respect to the volume at constant temperature.

58b. Diatomic Molecules.—In passing from a consideration of atoms to that of molecules, it is convenient to discuss first the properties of diatomic molecules. The internal partition function now includes contributions from one vibrational and two rotational degrees of freedom, in addition to the factors due to electronic and nuclear spin degeneracies. In general, the effect of electronic levels above the ground state can be neglected, since the energy of even the first excited state is usually so high that it makes a negligible contribution to the partition function except at very high temperatures. The frequency separation between the lowest and first excited states of the oxygen molecule is probably one of the smallest for any diatomic molecule, namely 7881 cm^{-1} , yet the latter does not contribute appreciably to the partition function at temperatures below about 2000° K . For other molecules, therefore, still higher temperatures would be necessary before excited electronic states made any noticeable contribution to the partition function. Consequently, it is evident that for all ordinary purposes, any electronic state of a diatomic molecule above the ground state can be neglected. Nearly all stable molecules, with the notable exceptions of oxygen,

sulfur (S_2), and nitric oxide, which will be considered later, have $^1\Sigma$ ground terms. The lowest states of such molecules are thus singlets, and the value of Q_e , the electronic partition function, is unity. For the majority of stable diatomic molecules, the situation as regards the electronic contribution is thus very simple. As just mentioned, a few stable molecules and, in addition, a number of radicals, such as CN and OH, do not have $^1\Sigma$ ground states; these substances require special treatment which will be deferred for the present.

58c. Separation of Internal Partition Function.—Because of the relationship between nuclear spin and rotational levels (cf. Section 31), it is convenient to include the nuclear spin factor with the rotational contribution to the partition function. For the present, therefore, the internal partition function of a stable diatomic molecule may be regarded as made up solely of the contributions from rotational and vibrational degrees of freedom. If the rotational and vibrational energies of a molecule are quite independent, then the energy ϵ_i due to internal degrees of freedom would be equal to the sum of ϵ_r , the rotational energy, and ϵ_v , the vibrational energy. It can be seen, therefore, by means of arguments similar to those used previously, that the internal partition function of a stable diatomic molecule can be separated into two parts, one Q_r for rotational, and the other Q_v for vibrational, degrees of freedom; thus,

$$Q_i = Q_r Q_v, \quad (58.4)$$

where

$$Q_r = \sum g_r e^{-\epsilon_r/kT} \quad \text{and} \quad Q_v = \sum g_v e^{-\epsilon_v/kT}.$$

The determination of the partition function for internal degrees of freedom, in a case of this type, resolves itself into the evaluation of the separate partition functions for rotation and vibration.

It will be observed that the expressions for all the thermodynamic quantities, viz., entropy, total energy, heat content, heat capacity, free energy and the maximum work function, involve either the logarithm of the partition function, or a derivative of this logarithm. Since the total partition function may be resolved into the *product* of the partition functions for various degrees of freedom, assuming that the respective energies are independent of each other, it is obvious that the thermodynamic quantities may be represented as the *sum* of the contributions of the separate degrees of freedom. As it is sometimes convenient to consider the effect of rotational and vibrational energies individually, it is of interest to see how the separation of the thermodynamic quantities can be made.

58d. Rotational and Vibrational Energies.—The expressions for the various parts of the total energy and heat capacity present no difficulty; taking the complete partition function Q , for a single molecule, as the product of the translational (Q_t), rotational (Q_r) and vibrational (Q_v) contributions, so that

$$Q = Q_t Q_r Q_v, \quad (58.5)$$

and

$$\ln Q = \ln Q_t + \ln Q_r + \ln Q_v,$$

it follows that the general equation (56.13) for the total energy per mole can be written as

$$E = RT^2 \left(\frac{\partial \ln Q_t}{\partial T} \right)_V + RT^2 \left(\frac{\partial \ln Q_r}{\partial T} \right)_V + RT^2 \left(\frac{\partial \ln Q_v}{\partial T} \right)_V. \quad (58.6)$$

The first term on the right-hand side is, of course, the translational energy, and the second and third terms represent the contributions to the total energy of the one mole of ideal gas made by the rotational and vibrational degrees of freedom, respectively. Since the partition functions for rotation and vibration are independent of the volume of the vessel occupied by the gas, the subscript V may be omitted; it is thus possible to write

$$E_r = RT^2 \frac{d \ln Q_r}{dT} \quad \text{and} \quad C_r = \frac{d}{dT} \left(RT^2 \frac{d \ln Q_r}{dT} \right) \quad (58.7)$$

and

$$E_v = RT^2 \frac{d \ln Q_v}{dT} \quad \text{and} \quad C_v = \frac{d}{dT} \left(RT^2 \frac{d \ln Q_v}{dT} \right), \quad (58.8)$$

where C_r and C_v are the rotational and vibrational contributions to the molar heat capacity. Since the respective partition functions are independent of pressure or volume, these degrees of freedom make the same contributions to the heat capacities at both constant pressure and volume.

58e. Entropy Due to Internal Degrees of Freedom.—With the entropy the situation is not so simple, and hence it requires more detailed examination; it will be seen that equation (56.12), for example, contains the term $-k \ln N!$, and it must be decided what is to be done with this when the total entropy is divided into its separate parts. It will be apparent from equation (55.33) that the $-k \ln N!$ term appears in the expression for the entropy of a monatomic molecule which, apart from possible nuclear spin and electronic contributions, is entirely translational in character; further, the same term is also found in equation (57.9) for the translational entropy. It would seem, therefore, that the corresponding relationship for the entropy associated with internal degrees of freedom should take the form

$$S_i = R \ln Q_i + RT \frac{d \ln Q_i}{dT} \quad (58.9)$$

where the suffix i may be taken to represent either the combined or separated internal, i.e., rotational and vibrational, degrees of freedom. This expression would also give the contribution to the entropy due to the nuclear spin, if, as is often the case, it is desired to separate this from the rotational entropy.

58f. Localized Elements.—It will not be out of place to refer briefly to the physical significance of the fact that the whole of the $-k \ln N!$ term is included with the translational entropy. A general consideration of the arguments already developed will show that this term has its origin in the indistinguishability of the N identical molecules that constitute a given system. Because the molecules are not distinguishable, although the Maxwell-Boltzmann statistics implies that they are, it is necessary to divide the total number of eigenstates by $N!$ as mentioned in Section 50j; the result is that the entropy is reduced by $k \ln N!$. As long as the particles are in motion it is not possible to distinguish between them, and the term $-k \ln N!$ must be included in the entropy. However, if the atoms or molecules are fixed in space, for example, as in a crystal lattice, it is possible, in principle, to identify each unit by its position in the space lattice. A system of this type would consist of what has been called *localized elements*, and the constituent atoms or molecules are to be regarded as distinguishable. For such systems the Maxwell-Boltzmann distribution law is applicable in its original form, provided the temperatures are reasonably high. In deriving an expression for the entropy of a system of localized elements the term $-k \ln N!$ would thus be omitted. If a system of molecules possessed only rotational or vibrational energy, or both, and no translational energy, it might be treated as a system of localized elements in the sense just considered. The separation of the energy of a system into two entirely independent parts, viz., internal and translational, thus permits the particles to be regarded as indistinguishable, as far as the translational entropy is concerned, but as distinguishable, localized elements, when the rotational and vibrational contributions are being considered.

59a. The Rotational Partition Function.—If the vibrational and rotational energies of a molecule are treated, as a first approximation, as being independent, the diatomic molecule may be considered as a rigid rotator with free axis. The rotational energy for a single molecule is then given by equation (9.68); for the present purpose, as in Chapter IV, it may be written as

$$\epsilon_r = J(J + 1) \frac{h^2}{8\pi^2 I}, \quad (59.1)$$

where I is the moment of inertia of the diatomic molecule. The rotational quantum number J can have zero or integral values. As in Section 28, this expression for the energy may be put in the form

$$\epsilon_r = J(J + 1) B h c, \quad (59.2)$$

where B is equal to $h/8\pi^2 I c$, and c is the velocity of light. It was also seen in Section 12 that for every value of J there are $2J + 1$ eigenstates corresponding to approximately the same magnitude of the rotational energy; each rotational level thus has a degeneracy of $2J + 1$. The expression for

the rotational partition function of a single molecule is consequently

$$\begin{aligned} Q_r &= \sum g_r e^{-\epsilon_r/kT} \\ &= \sum_{J=0}^{\infty} (2J+1) e^{-J(J+1)h^2/8\pi^2IkT} \\ &= \sum_{J=0}^{\infty} (2J+1) e^{-J(J+1)Bhc/kT} \end{aligned} \quad (59.3)$$

ignoring, for the present, the effect of the nuclear spin. If the symbol ρ is defined in the following manner,

$$\rho = \frac{Bhc}{kT} = \frac{h^2}{8\pi^2IkT}, \quad (59.4)$$

it is seen that the rotational partition function may be expressed as

$$Q_r = \sum_{J=0}^{\infty} (2J+1) e^{-J(J+1)\rho}. \quad (59.5)$$

The result of this summation can be obtained with a fair degree of accuracy by means of the Euler-Maclaurin formula; if ρ is less than unity, as will be the case at all temperatures above the very lowest, with the possible exception of very light molecules, such as hydrogen and deuterium, then

$$Q_r = \frac{1}{\rho} \left(1 + \frac{\rho}{3} + \frac{\rho^2}{15} + \frac{4\rho^3}{315} + \dots \right).$$

If ρ is quite small, e.g., less than 0.05, which will be true for nearly all substances at moderately high or high temperatures, all terms beyond the first in the parentheses may be neglected, so that the rotational partition function of a rigid diatomic molecule is given by

$$Q_r = \frac{1}{\rho} = \frac{8\pi^2IkT}{h^2}. \quad (59.6)$$

The same result can be derived in an alternative manner; equation (59.5) may be written as

$$Q_r = e^{\rho/4} \sum_{J=0}^{\infty} 2(J + \frac{1}{2}) e^{-(J+\frac{1}{2})^2\rho},$$

and if ρ is small, summation can be replaced by integration so that

$$Q_r = 2e^{\rho/4} \int_0^{\infty} (J + \frac{1}{2}) e^{-(J+\frac{1}{2})^2\rho} dJ,$$

Utilizing standard integrals, this becomes

$$Q_r = e^{\rho/4} \frac{1}{\rho} \approx \frac{1}{\rho},$$

and if ρ is small, $e^{\rho/4}$ is virtually unity, so that the result is the same as given by equation (59.6).

It is of interest to show that this approximate partition function, applicable at high temperatures which represent correspondence principle limits, can be obtained by utilizing the classical definition of the partition function, equation (57.8). The energy of a rotator with free axis, expressed in Hamiltonian form, is

$$H(p, q) = \frac{1}{2I} \left(p_\theta^2 + \frac{p_\phi^2}{\sin^2 \theta} \right), \quad (59.7)$$

and since the diatomic molecule has two rotational degrees of freedom, the classical partition function can be expressed as

$$Q_r = \frac{1}{h^2} \int \int \int \int e^{-(p_\theta^2 + p_\phi^2 / \sin^2 \theta) / 2IkT} dp_\theta dp_\phi d\theta d\phi \quad (59.8)$$

$$= \frac{1}{h^2} \int_{-\infty}^{\infty} e^{-p_\theta^2 / 2IkT} dp_\theta \int_{-\infty}^{\infty} e^{-p_\phi^2 / 2IkT \sin^2 \theta} dp_\phi \int_0^\pi d\theta \int_0^{2\pi} d\phi. \quad (59.9)$$

The first two integrals are standard forms, and so it is readily found that

$$\begin{aligned} Q_r &= \frac{2\pi IkT}{h^2} \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi \\ &= \frac{8\pi^2 IkT}{h^2}, \end{aligned}$$

in agreement with equation (59.6).

The contribution of rotational degrees of freedom to the total energy and heat capacity of a diatomic molecule may be obtained by combining the foregoing result with equations (58.7). Since

$$\frac{d \ln Q_r}{dT} = \frac{1}{T},$$

it follows that

$$E_r = RT \quad \text{and} \quad C_r = R. \quad (59.10)$$

This is just the contribution for two degrees of freedom to be expected from the classical principle of the equipartition of energy (Section 49c).

59b. Nuclear Spin Effects.—As already seen, every atomic nucleus having i units of spin can have $2i + 1$ orientations of almost identical energy; the statistical weight (degeneracy) due to the different orientations of the nuclei in a diatomic molecule is thus $(2i + 1)(2i' + 1)$, where i and i' are

the spins of the two nuclei. This result is strictly true for a heteronuclear molecule, that is one with two different nuclei; for such a diatomic molecule the complete rotational partition function, including the nuclear spin contribution, at reasonable temperatures would then be given by

$$Q_r = (2i + 1)(2i' + 1) \frac{8\pi^2 I k T}{h^2}. \quad (59.11)$$

A homonuclear substance, that is one with two identical nuclei, can exist in ortho and para states, which have different statistical weights, as shown in Section 31e. The statistical weight of the ortho states is $(i + 1)(2i + 1)$, whereas that of the para states is $i(2i + 1)$, the sum being $(2i + 1)(2i + 1)$, as is to be expected. As already seen, the rotational levels associated with the two states depend on the particular statistics followed by the nuclei and on various symmetry considerations. For molecules in $^1\Sigma_g^+$ states, e.g., hydrogen and deuterium in their ground states, the Fermi-Dirac statistics are obeyed if the atomic mass numbers are odd, while the Bose-Einstein statistics are followed if the atomic mass numbers are even. In the former case, the ortho states are associated with odd values of the rotational quantum number J , while the para states have even values of J ; in the latter case, the situation is reversed.

For homonuclear Σ_g^+ molecules obeying the Fermi-Dirac statistics, e.g., hydrogen, the complete rotational partition function is

$$Q_r = i(2i + 1) \sum_{J=0, 2, 4, \dots}^{\infty} (2J + 1) e^{-J(J+1)\rho} \\ + (i + 1)(2i + 1) \sum_{J=1, 3, 5, \dots}^{\infty} (2J + 1) e^{-J(J+1)\rho}. \quad (59.12)$$

For homonuclear Σ_g^+ molecules obeying the Bose-Einstein statistics, e.g., deuterium, the complete rotational partition function is

$$Q_r = (i + 1)(2i + 1) \sum_{J=0, 2, 4, \dots}^{\infty} (2J + 1) e^{-J(J+1)\rho} \\ + i(2i + 1) \sum_{J=1, 3, 5, \dots}^{\infty} (2J + 1) e^{-J(J+1)\rho}, \quad (59.13)$$

where ρ is defined, as before, by

$$\rho = \frac{h^2}{8\pi^2 I k T}.$$

With the exception of the hydrogen and deuterium molecules, which will be treated more fully at a later stage, the quantity ρ for the majority, if not all, homonuclear diatomic molecules, is very small at all temperatures except the very lowest. Under these conditions, i.e., with $\rho \ll 1$, it is found

that apart from the nuclear spin factors, the summation included in the partition function when carried over the even values of the rotational quantum number, is equal to that for the odd values; thus

$$\sum_{J=0, 2, 4, \dots} (2J + 1)e^{-J(J+1)\rho} = \sum_{J=1, 3, 5, \dots} (2J + 1)e^{-J(J+1)\rho}. \quad (59.14)$$

The total summation over all the values of J , both odd and even, is equal to $1/\rho$, as seen by equation (59.6); hence each sum over either odd or even J values is equal to $1/2\rho$. It follows, therefore, from equations (59.12) and (59.13), irrespective of which type of statistics is obeyed, that

$$\begin{aligned} Q_r &= \frac{i(2i + 1)}{2\rho} + \frac{(i + 1)(2i + 1)}{2\rho} \\ &= \frac{(2i + 1)^2}{2\rho} \\ &= (2i + 1)^2 \frac{8\pi^2 I k T}{2h^2}, \end{aligned} \quad (59.15)$$

provided the conditions are such that ρ is small.

Comparison of this result with equation (59.11), for a heteronuclear molecule, shows that the two rotational partition functions are similar, but a factor of $\frac{1}{2}$ appears in the case of a homonuclear molecule. As derived here, this factor is the result of using quantum statistics, which require a distinction to be made between ortho and para states, but the necessity for its introduction was realized even in classical statistical mechanics. A homonuclear molecule can occupy two equivalent orientations in space as a result of simple rotation; since the two nuclei are identical, the two equivalent orientations are indistinguishable, and the number of elementary cells in phase (γ) space occupied by the system is reduced by a factor of two, as compared with the case of a diatomic molecule with dissimilar nuclei. This decrease of volume in phase space, and hence in the probability of the occurrence of the system of homonuclear molecules, results in the introduction of the factor $\frac{1}{2}$ in the partition function on the basis of the classical statistics.

59c. The Symmetry Number.—In general, if any molecule containing two or more atoms can take up σ equivalent orientations in space as the result of simple rotation, that molecule is said to have a *symmetry number* equal to σ ; the partition function derived classically must then be divided by this symmetry number to give the correct value. The quantum statistical calculations of the partition function include this factor automatically. The general expression for the rotational partition function of any rigid diatomic molecule, homonuclear or heteronuclear, at moderately high temperatures, is then

$$Q_r = (2i + 1)(2i' + 1) \frac{8\pi^2 I k T}{\sigma h^2}. \quad (59.16)$$

For a heteronuclear molecule σ is unity, and the result becomes identical with equation (59.11); if the molecule is homonuclear, i and i' are equal, and σ is equal to 2, so that the expression reduces to the same form as equation (59.15). Attention may be called to the fact that a molecule is to be regarded as homonuclear only if both nuclei are isotopically identical; if the two atoms are of the same element, but are different isotopes, e.g., HD, the molecule is not to be treated as homonuclear.

59d. Rotation and Entropy.—Combination of equation (59.16) with the general expression for the rotational entropy, equation (58.9), gives the result, for correspondence principle limits,

$$S_r = R \ln (2i + 1)(2i' + 1) + R \ln \frac{8\pi^2 I k T}{\sigma h^2} + R. \quad (59.17)$$

The first term on the right-hand side represents the contribution to the entropy of the degeneracy resulting from the different possible orientations of the spinning atomic nuclei; it is consequently referred to as the *nuclear spin entropy*. When individual entropies are used, as they frequently are, to calculate entropy changes in a chemical reaction, the nuclear spin entropies will cancel, because there is no change either in the number or nature of the nuclei taking part in the reaction. The contribution of the products of the reaction to the nuclear spin entropy will thus be identical with that of the reacting molecules. For this reason, and because nuclear spins are not always known, it is the common practice to omit the nuclear spin entropy; the result is called the *virtual entropy* or the *practical entropy*. This practice applies to molecules of all types, monatomic, diatomic or polyatomic. If it is required to obtain the total entropy, the nuclear spin entropy, given by $R \ln (2i_1 + 1)(2i_2 + 1) \cdots (2i_n + 1)$, where i_1, i_2, \dots, i_n are the spins of the various atoms making up the molecule, must be added to the practical entropy. On the other hand, if the total entropy is known, the practical entropy may be derived from it by subtraction of the nuclear spin contribution. It should be emphasized that the symmetry number of the molecule is still retained in the expression for the rotational entropy; this must on no account be omitted, for symmetry is obviously not unchanged in a chemical reaction.

Attention may be called to the fact that the considerations of the foregoing paragraph, which permit the subtraction of the nuclear spin entropy, are applicable only if the ortho-para ratio of the system is equal to its limiting, high temperature, value and remains unchanged. This condition always holds, of course, for heteronuclear molecules, and for homonuclear molecules, with the exception of H_2 and D_2 , at all temperatures above the very lowest. For hydrogen and deuterium molecules the practical entropies may be used at temperatures above 300° and 200° K, respectively, provided ortho-para equilibrium exists in the system.

59e. Diatomic Molecules: Special Cases.—The few diatomic molecules that do not have $^1\Sigma$ ground terms present special cases which may be con-

sidered briefly. The lowest state of molecular oxygen $^{16}\text{O}^{16}\text{O}$ is a $^3\Sigma_g^-$ term, and as the energy separations of the levels of the triplet are very small, these levels may be regarded as having the same energy. The value of J to be used in calculating the statistical weights are equal to $K + 1$, K and $K - 1$, respectively (cf. Section 30e), for the three levels, generally designated by the symbols F_1 , F_2 and F_3 . Because the molecule is homonuclear and the nuclear spin is zero, alternate rotational levels are absent; those present correspond to odd values only of K . The degeneracies $(2J + 1)$ of the corresponding levels in the F_1 , F_2 and F_3 series are thus $2K + 3$, $2K + 1$ and $2K - 1$, respectively, with K equal to 1, 3, 5, etc. Since the spin of the oxygen nucleus is zero, the nuclear spin degeneracy $(i + 1)(2i + 1)$ is equal to unity. The complete rotational partition function for molecular oxygen may thus be written in the form of the three summations, viz.,

$$Q_r = \sum_{K=1, 3, 5, \dots} (2K + 3)e^{-\epsilon_{F_1(K)}/kT} + \sum_{K=1, 3, 5, \dots} (2K + 1)e^{-\epsilon_{F_2(K)}/kT} + \sum_{K=1, 3, 5, \dots} (2K - 1)e^{-\epsilon_{F_3(K)}/kT}.$$

Although it is not the case at ordinary temperatures, at relatively high temperatures, when a large number of terms make appreciable contributions to the total, the three summations become equal; further, since only alternate rotational levels are present, each of the summations will be equal to $\frac{1}{2}p$. Under these conditions, therefore it can be seen that

$$Q_r = \frac{3}{2p} = 3 \frac{8\pi^2 I k T}{2h^2},$$

or, in general,

$$Q_r = g_e \frac{8\pi^2 I k T}{\sigma h^2},$$

where g_e is the electronic statistical weight, i.e., 3, and σ is the symmetry number, i.e., 2.

For diatomic molecules that have other than Σ ground states, it is necessary to take into account the degeneracy known as Λ -type doubling (Section 30f), in addition to other types of degeneracy. Nitric oxide, for example, has a $^2\Pi_{1/2, 3/2}$ ground term; for the lower level of the doublet the smallest value of J , which is here also the rotational quantum number (Hund's case (a)), is $\frac{1}{2}$, whereas for the upper level it is $\frac{3}{2}$, the subsequent values increasing in steps of unity. The spins of the nitrogen and oxygen nuclei are 1 and 0, respectively; the statistical weight $(2i + 1)(2i' + 1)$ due to nuclear spin is thus 3. The complete rotational partition function of nitric oxide is then represented by

$$Q_r = 2 \times 3 \sum_{J=1/2, 3/2, 5/2, \dots} (2J + 1)e^{-\epsilon_J/kT} + 2 \times 3 \sum_{J'=3/2, 5/2, 7/2, \dots} (2J' + 1)e^{-\epsilon_{J'}/kT},$$

where 2 and 3 are the Λ -type doubling and nuclear spin factors, respectively; ϵ_J and $\epsilon_{J'}$ refer to the rotational energies in the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ levels, for

various values of the rotational quantum numbers J and J' , respectively. Since the frequency separation of the nitric oxide doublets is quite appreciable, about 120 cm.^{-1} , it is evident that the two summations cannot become exactly equal. However, by taking the factor $e^{-120hc/kT}$ out of the contribution of the $^2\Pi_{1/2}$ state, the two sums become equal at moderately high temperatures. The rotational partition function for nitric oxide may then be written as

$$Q_r = \frac{2 \times 3}{\rho} (1 + e^{-120hc/kT})$$

$$= g_e g_n \frac{8\pi^2 I k T}{h^2},$$

where g_e , equal to $2(1 + 120e^{-hc/kT})$, is the product of the electron multiplicity and the Λ -type doubling factors, and g_n is the nuclear spin factor.

From the foregoing results it is possible to write a general equation for the complete rotational partition function of any rigid diatomic molecule, provided the temperature is relatively high, viz.,

$$Q_r = g_e g_n \frac{8\pi^2 I k T}{\sigma h^2}. \quad (59.18)$$

The nuclear spin factor g_n is equal to $(2i + 1)(2i' + 1)$, and σ is 2 for a homonuclear molecule and 1 for a heteronuclear molecule. The electronic factor g_e , which is strictly speaking the electronic partition function, must include the allowance, if necessary, for Λ -type doubling and for the separation between the corresponding levels of multiplets.

60a. The Vibrational Partition Function.—The vibrational energy of a linear harmonic oscillator is given by equation (29.1), as

$$\epsilon_v = (v + \frac{1}{2})hc\omega, \quad (60.1)$$

where $\omega \text{ cm.}^{-1}$ is the vibration frequency, and v is the quantum number which can have the values 0, 1, 2, etc. As explained in Section 56e, the energy generally employed in the evaluation of the partition function is based on that of the lowest level as zero; in the present case the energy of the lowest ($v = 0$) level is $\frac{1}{2}hc\omega$, and so the vibrational energy to be used is given by

$$\epsilon_v = (v + \frac{1}{2})hc\omega - \frac{1}{2}hc\omega$$

$$= vhc\omega.$$

The statistical weight of each vibrational energy level of different frequency is unity, and hence the vibrational partition function of a single molecule is

$$Q_v = \sum_v g_v e^{-\epsilon_v/kT}$$

$$= \sum_{v=0}^{\infty} e^{-vhc\omega/kT}. \quad (60.2)$$

If $hc\omega/kT$ is replaced by x , the partition function becomes

$$Q_v = \sum_{v=0}^{\infty} e^{-vx} = 1 + e^{-x} + e^{-2x} + \dots$$

$$= (1 - e^{-x})^{-1}.$$

The general equation for the partition function of a harmonic oscillator is thus

$$Q_v = (1 - e^{-hc\omega/kT})^{-1}. \quad (60.3)$$

The total energy E_v of a harmonic oscillator may be obtained with the aid of equation (58.8); utilizing the vibrational partition function in the form of equation (60.3), the result per mole is

$$E_v = RT^2 \frac{d \ln Q_v}{dT}$$

$$= \frac{RT}{e^{hc\omega/kT} - 1} \cdot \frac{hc\omega}{kT} = RT \frac{x}{e^x - 1}. \quad (60.4)$$

This equation gives the vibrational energy per mole with reference to the energy of the lowest (zero-point) level; if the total energy is required, the zero-point energy E_0 , equal to $\frac{1}{2}Nhc\omega$, must be added to the value of E_v according to equation (60.4).

Differentiation of E_v , with or without E_0 added, with respect to temperature gives the vibrational contribution to the heat capacity; thus

$$C_v = \frac{d}{dT} \left(RT^2 \frac{d \ln Q_v}{dT} \right)$$

$$= \frac{R e^{hc\omega/kT}}{(e^{hc\omega/kT} - 1)^2} \left(\frac{hc\omega}{kT} \right)^2 = R \frac{e^x x^2}{(e^x - 1)^2}. \quad (60.5)$$

It may be remarked that the functions of x in equations (60.4) and (60.5), referred to as *Einstein functions*, have been calculated and tabulated for various values of x , i.e., of $hc\omega/kT$; these tables greatly facilitate the calculation of vibrational energies and heat capacities.

The vibrational entropy per mole can be obtained by means of equation (58.9); thus

$$S_v = RT \frac{d \ln Q_v}{dT} + R \ln Q_v$$

$$= \frac{R}{e^{hc\omega/kT} - 1} \cdot \frac{hc\omega}{kT} - R \ln (1 - e^{-hc\omega/kT}). \quad (60.6)$$

At moderate temperatures, $hc\omega/kT$, i.e., x , is relatively large for many stable diatomic molecules, e.g., hydrogen, deuterium, oxygen and nitrogen;

when this is the case, both e^x and $e^x - 1$ are very large. It can be seen from equation (60.4) that the vibrational energy E_v is then very small. This means that at moderate temperatures practically all the molecules are in their lowest vibrational level, that is, the one for which v is zero. It will be observed that under these conditions the vibrational partition function as given by equation (60.3) is very close to unity. As the temperature increases, the value of $hc\omega/kT$ decreases, and hence $e^x - 1$ becomes smaller; the vibrational energy should thus increase as the temperature is raised. The physical significance of this fact is that at higher temperatures an increasing number of molecules occupy the higher vibrational levels, for which the quantum number v is greater than zero. At relatively high temperatures, $hc\omega/kT$ is small enough for $e^x - 1$ to be virtually equal to x ; in these circumstances, the energy E_v given by equation (60.4) is equal to RT . The contribution of the vibrational degrees of freedom to the total energy at high temperatures is thus virtually equal to RT , which is the classical equipartition value for energy, such as vibrational, expressible in two square terms (Section 49c). Since e^x is approximately equal $1 + x$ at relatively high temperatures, the vibrational partition function becomes equal to $1/x$, i.e., to $kT/hc\omega$.

It is evident from the variation of the vibrational contribution to the total partition function that the vibrational heat capacity will be zero at low and moderate temperatures, and will increase to a maximum of R , which is the classical value, as the temperature is raised. From these considerations, it is a simple matter to explain the fact that the molar heat capacity of a diatomic gas is generally appreciably less than the classical value at ordinary temperatures, but increases toward this value as the temperature is raised. At the lower temperatures nearly all the molecules are in their lowest ($v = 0$) vibrational level, and the vibrational energy, in excess of the zero-point value, is zero; the contribution to the heat capacity is thus also zero. The latter is then made up solely of the translational ($\frac{3}{2}R$) and rotational (R) contributions, both of which become classical at relatively low temperatures. The total heat capacity at constant volume, at moderate temperatures, should thus be about $\frac{5}{2}R$, as is actually found for hydrogen, oxygen, nitrogen, etc. As the temperature is raised, more and more of the molecules occupy higher vibrational levels, and at sufficiently high temperatures the contribution to the heat capacity increases to R . The total heat capacity at constant volume should then approach $\frac{7}{2}R$. Attention may be called to the fact that the molar heat capacity of chlorine at ordinary temperatures is about 6 cal.; this means that some of the higher vibrational levels of this molecule are then occupied. The reason is that the vibration frequency ω of the atoms in the chlorine molecule, 565 cm.^{-1} , is much smaller than for the other diatomic molecules.

60b. Classical Vibrational Partition Function.—The calculation of the classical vibrational partition function is of interest because it brings out clearly the superiority of the quantum mechanical treatment. The total

energy of a diatomic harmonic oscillator in Hamiltonian form is

$$H(p, q) = \frac{p^2}{2\mu} + \frac{fq^2}{2}, \quad (60.7)$$

where μ is the reduced mass of the oscillator, and f is the restoring force per cm. displacement. Since a diatomic oscillator possesses one degree of freedom, the classical vibrational partition function is

$$\begin{aligned} Q_v &= \frac{1}{h} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-H(p, q)/kT} dp dq \\ &= \frac{1}{h} \int_{-\infty}^{\infty} e^{-p^2/2\mu kT} dp \int_{-\infty}^{\infty} e^{-fq^2/2kT} dq \\ &= \frac{kT}{h} \cdot 2\pi \sqrt{\frac{\mu}{f}}. \end{aligned} \quad (60.8)$$

The frequency ν sec.⁻¹ of a harmonic oscillator is related to the reduced mass and the restoring force by the expression (cf. Section 29g)

$$\nu = \frac{1}{2\pi} \sqrt{\frac{f}{\mu}},$$

and introduction of this result into equation (60.8) leads to

$$Q_v = \frac{kT}{h\nu} = \frac{kT}{hc\omega}, \quad (60.9)$$

where ω , equal to ν/c , is the frequency in cm.⁻¹. This is seen to be the same as the high temperature limiting value of the partition function derived by the quantum method. However, whereas the latter allows for the variation in the extent of the vibrational contribution to the energy and heat capacity with temperature, the classical expression requires E_v to be always equal to RT , and C_v to R ; as noted above, this is not in agreement with experiment.

In a sense, of course, the classical method always fails to represent adequately the actual behavior of a system, but for translational and rotational degrees of freedom the energy quanta, or separations of successive levels, are so small that many of these levels are occupied at ordinary temperatures. The departure from classical behavior is therefore not very apparent, although it would be observed more definitely in connection with measurements at low temperatures. With vibrational energy, on the other hand, the energy separation of successive levels is quite large, and hence the molecules are distributed over very few levels at ordinary temperatures. The conditions are thus relatively remote from the correspondence principle limits, and the deficiency of the classical treatment is manifest. At high temperatures, the actual value depending on the magnitude of the energy separation, the higher vibrational levels are occupied to an appreciable extent, and the system approaches classical behavior.

61a. Combined Partition Functions: Nonrigid Diatomic Molecules.⁵—

The treatment of the preceding sections has been based on the assumption that vibrational and rotational energies are independent; in other words, the approximation has been made of taking the molecule to be rigid, in spite of the fact that it vibrates. As seen in Section 29e, allowance must always be made for the interaction of vibrational and rotational energies, and this can be done by the use of equation (29.26); the combined energies, in the ground state of a molecule, may then be represented by ⁶

$$\epsilon_{vJ} = (v + \frac{1}{2})hc\omega_e - (v + \frac{1}{2})^2hc x\omega_e + \dots \\ + B_v J(J+1)hc - D_v J^2(J+1)^2hc + \dots \quad (61.1)$$

The combined rotational and vibrational partition function, apart from nuclear spin and symmetry factors, for a $^1\Sigma$ molecule, is thus given by the double summation

$$Q_{vr} = \sum_{v=0}^{\infty} \sum_{J=0}^{\infty} (2J+1)e^{-\epsilon_{vJ}/kT}, \quad (61.2)$$

where ϵ_{vJ} is given by equation (61.1). Since the various constants ω_e , x , B_v , D_v , etc., can be obtained from spectroscopic data, as seen in Chapter IV, the complete evaluation of Q_{vr} is possible, at least in principle. The summation is first carried out over all J values for $v = 0$, and then the process is repeated for $v = 1, 2, 3$, etc., and the separate sums are added together. If the temperature is not high, e.g., 300° K, virtually all the molecules are in the lowest vibrational levels, i.e., $v = 0, 1$ and 2 , and so the calculations are restricted to these levels. Since the separations of rotational levels are small, an appreciable number of such levels are occupied even at ordinary temperatures, and hence the summation may have to be carried over a large number of J values. For light molecules, i.e., those of small moment of inertia, such as hydrogen and deuterium molecules, the rotational quanta are relatively large, and few rotational levels are occupied; the evaluation of the rotational sum, for the various possible J values, is then simple, since few terms are concerned.

For relatively heavy molecules and high temperatures there are so many terms involved in both rotational and vibrational sums, that the process of summation becomes extremely tedious. In order to avoid the labor involved, various mathematical devices have been developed which permit a very considerable simplification in the evaluation of the partition function. The procedure adopted is first to devise an equation for the sum over the rotational states, using an expression of the type

$$\epsilon_r = B_v J(J+1)hc - D_v J^2(J+1)^2hc + \dots$$

⁵ Giauque and Overstreet, *J. Am. Chem. Soc.*, **54**, 1731 (1932); Johnston and Davis, *ibid.*, **56**, 271 (1934); Gordon and Barnes, *J. Chem. Phys.*, **1**, 297 (1933); Kassel, *ibid.*, **1**, 576 (1933); **3**, 115 (1935); ref. 3; Gordon, *J. Chem. Phys.*, **2**, 65 (1934); **3**, 259 (1935).

⁶ For convenience in connection with the summation over the v and J values in equation (61.2), the symbol ϵ_{vJ} is used here instead of ϵ_{vr} .

for the rotational part of the energy of a nonrigid molecule. A further stage in the treatment provides a formula for the summation over the vibrational levels of the molecule. The calculations can, in certain cases, be simplified by the use of tabulated values of functions that appear in the final expression for the rotational-vibrational partition function. Several summation procedures have been developed; originally the forms were applicable to $^1\Sigma$ molecules, but they have been extended to $^2\Pi$ and $^3\Sigma$ molecules. Since the formulas giving the total energy, heat capacity and entropy involve the first and second derivatives of the partition function with respect to temperature, expressions for these quantities have also been developed.

61b. Approximate Partition Functions.—For most diatomic molecules, at temperatures that are not too low or too high, a simple approximate treatment gives partition functions that are sufficiently accurate for many purposes. The rotational and vibrational energies are treated as independent; the rotational contribution to the partition function is then taken as the classical value, given by equation (59.18), whereas the vibrational contribution is that for a quantized, harmonic oscillator, as defined by equation (60.3). The translational partition function, as in all cases, is represented by equation (57.5) or (57.6), so that a fair approximation to the complete partition function for the diatomic molecule is

$$Q = g_e g_n \left\{ \frac{(2\pi m k T)^{3/2}}{h^3} \cdot \frac{RT}{P} \right\} \left(\frac{8\pi^2 I k T}{\sigma h^2} \right) (1 - e^{-hc\omega/kT})^{-1}. \quad (61.3)$$

Since most stable diatomic molecules have $^1\Sigma$ ground terms, the electronic factor g_e is unity; the nuclear spin statistical weight g_n is $(2i + 1)(2i' + 1)$, but this can be omitted except for a process involving a change of ortho-para ratio. The symmetry number σ , which is 2 for a homonuclear molecule, must always be included, as already mentioned.

In order to indicate the degree of accuracy attainable with equation (61.3), some data will be quoted. For molecular oxygen $^{16}\text{O}^{16}\text{O}$, for example, the partition function derived in this manner, using spectroscopic data for the moment of inertia and the vibration frequency is 216.4 at 298.16° K. The corresponding result obtained by careful summation over the individual vibrational and rotational energy levels, and allowing for anharmonicity and interaction, is 219.99. Similarly, for hydrogen chloride, the respective values for the partition function are 19.85 and 20.18. Since the expressions for certain thermodynamic functions, such as entropy and energy, involve the logarithm of the partition function, with or without its derivative with respect to temperature, small discrepancies between the accurate and approximate partition functions are not serious (see, however, Section 63d). It follows, therefore, that for many purposes equation (61.3) may be utilized for the calculation of the thermodynamic properties of a diatomic molecule. The errors are greater at temperatures of the order of 1000° K or higher, and also at very low temperatures. If data are required under such conditions, then the detailed summation procedure, or its mathematical equivalent, must be employed.

62a. Polyatomic Molecules.—A molecule containing n atoms has $3n$ degrees of freedom; that is, $3n$ coordinates, using the term in a general sense, are required to specify the complete configuration of the molecule. Of these coordinates, three are the so-called external coordinates, which give the position of the center of gravity of the molecule in space. In general, except for diatomic and linear molecules, three coordinates, to which reference will be made shortly, are required to indicate the orientation of the molecule; this is equivalent to the statement that molecules, with the exceptions noted, have three rotational degrees of freedom. There are consequently $3n - 6$, coordinates still remaining to be specified to give the relative positions of the atoms and the centers of gravity of internally rotating groups. Assuming, for the present, that there are no groups in the molecule that exhibit internal rotation, the $3n - 6$ degrees of freedom represent vibrational modes. The orientation of a linear molecule in space can be represented by two coordinates, so that molecules of this type have but two degrees of rotational freedom; they consequently possess $3n - 5$ vibrational modes. If there are present in the molecule groups capable of undergoing free internal rotation, the number of degrees of vibrational freedom is reduced by the number of such rotations. In many cases the molecules possess elements of symmetry; in this event some of the vibrational modes are degenerate (cf. Section 34). In the evaluation of the partition function of a polyatomic molecule the foregoing facts must be taken into consideration.

After separating the translational degrees of freedom from those due to internal coordinates, in the usual manner, an exact evaluation of the partition functions of certain, relatively simple, polyatomic molecules has been achieved by the summation method. In most cases, however, the molecule has been treated as rigid, and the rotational and vibrational energies have been taken as independent. The combined rotational-vibrational partition function is then obtained as the product of the separate contributions of the rotational and vibrational degrees of freedom. The classification of polyatomic molecules according to their electronic configurations, as described in Chapter VI for diatomic molecules, is possible for a limited number of substances only; in other cases, it is assumed that the lowest electronic level of the molecule is a singlet state, and that excited states make no contribution to the total partition function. Unless there is evidence to the contrary, therefore, the electronic factor is unity; exceptions to this rule are molecules, such as nitrogen dioxide, containing an odd number of electrons.

62b. Rotational Partition Functions.—At all reasonable temperatures, the rotational levels of a polyatomic molecule, like those of diatomic molecules, are occupied in sufficient numbers for the behavior in respect of rotation to be virtually classical in character. In the derivation of the rotational contribution to the partition function of a polyatomic molecule, it is therefore adequate, and actually much simpler, to use the classical method of calculation. For this purpose it is most convenient to employ the so-called *Eulerian angles* to define the orientation in space of the molecule, assumed to be a rigid body, while three cartesian coordinates are used to determine

the position of its center of gravity. Let x, y, z , be the cartesian axes fixed in space, and X, Y, Z , the three principal axes, at right angles, within the molecule itself; both sets of axes are referred to the same origin O . The planes containing the axes xy and XY meet at the line ON , which is called the nodal line. The Eulerian angles θ, ϕ and ψ are then defined in the following manner. The angle θ is that between the body axis Z and the space axis z ; the angle between the nodal line and the x axis is ϕ . The third

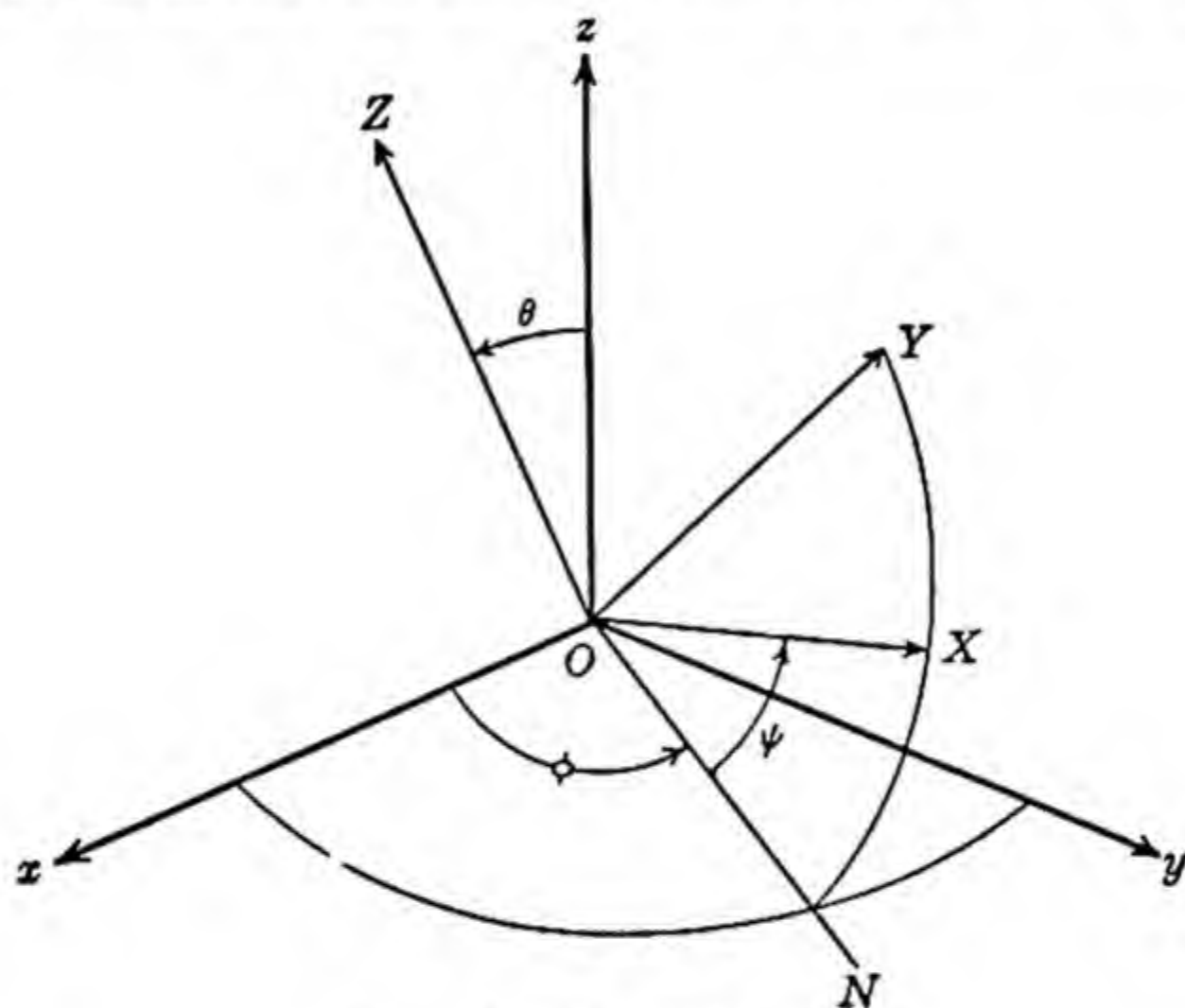


FIG. 41. Eulerian angles

angle ψ is the one between the nodal line and the X axis in the molecule (Fig. 41). These three angles define the orientation of the molecule with fixed center of gravity. The angle θ may vary between zero and π , while the other angles ϕ and ψ can vary from zero to 2π .

The rotational energy of the molecule is expressed in Hamiltonian form, that is, in terms of the Eulerian angles, θ, ϕ, ψ , and their conjugate momenta, p_θ, p_ϕ, p_ψ , by the equation

$$H(p, q) = \frac{\sin^2 \psi}{2A} \left\{ p_\theta - \frac{\cos \psi}{\sin \theta \sin \psi} (p_\phi - p_\psi \cos \theta) \right\}^2 + \frac{\cos^2 \psi}{2B} \left\{ p_\theta + \frac{\sin \psi}{\sin \theta \cos \psi} (p_\phi - p_\psi \cos \theta) \right\}^2 + \frac{1}{2C} p_\psi^2,$$

where A, B and C are the three principal moments of inertia of the molecule. For ease of integration, this expression is put into the alternative form

$$H(p, q) = \frac{1}{2} F \left\{ p_\theta + \frac{\sin \psi \cos \psi}{F \sin \theta} \left(\frac{1}{B} - \frac{1}{A} \right) (p_\phi - p_\psi \cos \theta) \right\}^2 + \frac{1}{2AB \sin^2 \theta} \cdot \frac{1}{F} (p_\phi - p_\psi \cos \theta)^2 + \frac{1}{2C} p_\psi^2, \quad (62.2)$$

where F is a function of ψ defined by

$$F = \frac{\sin^2 \psi}{A} + \frac{\cos^2 \psi}{B}.$$

The classical partition function for three rotational degrees of freedom is

$$Q_r = \frac{1}{h^3} \int_0^\pi \int_0^{2\pi} \int_0^{2\pi} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-H(p,q)/kT} d\theta d\phi d\psi dp_\theta dp_\phi dp_\psi, \quad (62.3)$$

the value of $H(p, q)$ being given by equation (62.2). The integration is first carried out with respect to p_θ , p_ϕ and p_ψ , in turn, making use of the fact that

$$\int_{-\infty}^{\infty} e^{-a(x+b)^2} dx = \int_{-\infty}^{\infty} e^{-ax^2} dx = \left(\frac{\pi}{a}\right)^{1/2}.$$

Integrating first over p_θ , there is obtained the factor $(2\pi kT/F)^{1/2}$; integration with respect to p_ϕ then gives $F^{1/2}(2\pi kTAB)^{1/2} \sin \theta$, while finally integration over p_ψ leads to the factor $(2\pi kTC)^{1/2}$; multiplication of these three factors yields $(2\pi kT)^{3/2}(ABC)^{1/2} \sin \theta$, so that

$$\begin{aligned} Q_r &= \frac{(2\pi kT)^{3/2}(ABC)^{1/2}}{h^3} \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi \int_0^{2\pi} d\psi \\ &= \frac{8\pi^2(8\pi^3 ABC)^{1/2}(kT)^{3/2}}{h^3}. \end{aligned} \quad (62.4)$$

The calculation, so far, has not taken into account molecular symmetry, or the nuclear spin statistical weight; allowance must, of course, always be made for the former, while the latter may be excluded if desired. The complete rotational partition function, including the nuclear spin factor, is thus

$$Q_r = g_n \frac{8\pi^2(8\pi^3 ABC)^{1/2}(kT)^{3/2}}{\sigma h^3}, \quad (62.5)$$

in which σ is the symmetry number, and g_n is equal to the product of the $2i + 1$ terms, where i is the nuclear spin, for every atom in the molecule. The symmetry numbers of some polyatomic molecules are as follows: H_2O and SO_2 (2); NH_3 (3); C_2H_4 (4); CH_4 and C_6H_6 (12).

If the moments of inertia A , B and C are known from spectroscopic data (cf. Section 35), the rotational partition function can be calculated directly from equation (62.5). Alternatively, if the molecular dimensions are known, e.g., from electron diffraction measurements, the product ABC may be derived from the determinant

$$ABC = \begin{vmatrix} I_{xx} & -I_{xy} & -I_{xz} \\ -I_{xy} & I_{yy} & -I_{yz} \\ -I_{xz} & -I_{yz} & I_{zz} \end{vmatrix} \quad (62.6)$$

where the moments of inertia I_{xx} , I_{yy} , I_{zz} are defined by

$$I_{xx} = \sum_i m_i (y_i^2 + z_i^2) \text{ etc.,}$$

and the products of inertia I_{xy} , I_{xz} , I_{yz} are given by

$$I_{xy} = \sum_i m_i x_i y_i, \text{ etc.,}$$

where m_i is the mass of the i th atom, and x_i , y_i , z_i are its coordinates in any system of cartesian coordinates whose origin coincides with the center of gravity of the molecule. The summations are in each case carried over the coordinates of all the atoms.

The contribution E_r to the total energy of a polyatomic molecule made by the rotational degrees of freedom may be derived from the partition function, given by equation (62.5), by making use of (58.7). It is readily seen that for 1 mole

$$\begin{aligned} E_r &= RT^2 \frac{d \ln Q_r}{dT} \\ &= \frac{3}{2} RT, \end{aligned}$$

which is in agreement, as it should be, with the classical value derived from the equipartition principle for a rotator with three degrees of freedom, i.e., with energy in three square terms. The contribution of the rotator to the molar heat capacity of the polyatomic molecule is obviously $\frac{3}{2}R$.

The general expression, equation (62.5), for the rotational partition function of any polyatomic molecule can be put in a simpler form. If ρ_A , ρ_B and ρ_C are defined in a manner similar to that employed previously for ρ [equation (59.4)], viz.,

$$\rho_A = \frac{h^2}{8\pi^2 A k T}; \quad \rho_B = \frac{h^2}{8\pi^2 B k T}; \quad \rho_C = \frac{h^2}{8\pi^2 C k T},$$

it is seen that

$$Q_r = \frac{g_n}{\sigma} \cdot \frac{\pi^{1/2}}{(\rho_A \rho_B \rho_C)^{1/2}}. \quad (62.7)$$

This is the equation applicable to all polyatomic molecules, and particularly to asymmetrical tops, for which A , B and C are different (cf. Section 35f); for planar molecules of this type, e.g., water and benzene, $A + B = C$.

For a symmetrical top molecule, two of the three moments of inertia, e.g., A and B , are equal while the third, i.e., C , is different; equation (62.7) then becomes

$$Q_r = \frac{g_n}{\sigma} \cdot \frac{\pi^{1/2}}{\rho_A \rho_C^{1/2}}. \quad (62.8)$$

If the three principal moments of inertia A , B and C are all equal, as for a

spherical molecule, the partition function for rotation is

$$Q_r = \frac{g_n}{\sigma} \cdot \frac{\pi^{1/2}}{\rho^{3/2}}. \quad (62.9)$$

As already seen, the orientation in space of a linear molecule can be defined by means of two coordinates; hence, such a molecule has only two degrees of rotational freedom. As far as rotation is concerned a linear molecule behaves like a diatomic molecule (cf. Section 35b), that is, as a rigid rotator with two identical moments of inertia. The rotational partition function is thus represented by the expression

$$Q_r = g_n \frac{8\pi^2 I k T}{\sigma h^2}. \quad (62.10)$$

The molecules HCN, N₂O, CO₂, COS, CS₂ and C₂H₂, are all linear, and to these equation (62.10) is applicable. For acetylene, carbon dioxide and carbon disulfide the symmetry number is 2, but in the other cases it is unity. The contribution to the total energy made by the two rotational degrees of freedom of a linear polyatomic molecule is found to be RT , as for a diatomic molecule.

62c. The Vibrational Partition Function.—As seen in Section 34b, the vibrational energy of a polyatomic molecule may be regarded as the sum of the energies corresponding to the various normal vibrations. If the energy is reckoned from that in the lowest vibrational level as zero, the total can be expressed by the sum

$$\epsilon_v = v_1 h c \omega_1 + v_2 h c \omega_2 + \cdots + v_i h c \omega_i + \cdots$$

where $\omega_1, \omega_2, \cdots, \omega_i, \cdots$, are the normal vibration frequencies, and $v_1, v_2, \cdots, v_i, \cdots$, are the quantum numbers. The vibrational partition function can then be written as

$$\begin{aligned} Q_v &= \sum_v e^{-\epsilon_v/kT} \\ &= \sum_{v_1} e^{-v_1 h c \omega_1/kT} \sum_{v_2} e^{-v_2 h c \omega_2/kT} \cdots \sum_{v_i} e^{-v_i h c \omega_i/kT} \cdots \end{aligned} \quad (62.11)$$

The vibrational partition function, as defined by equation (62.11), is the product of a number of sums, one for each of the vibrational modes of the molecule. It will be evident that each of the summation terms is of exactly the same form as the partition function of a diatomic molecule, equation (60.2); hence each of the terms is equivalent to (60.3), and the vibrational partition function for the polyatomic molecule may be written in the form

$$Q_v = \prod_i (1 - e^{-h c \omega_i/kT})^{-1}. \quad (62.12)$$

The number of terms included in the product depends on the number and nature of the normal vibrations. For a nonlinear polyatomic molecule there

are $3n - 6$ vibrational modes, and if these are all nondegenerate, the vibrational partition function will consist of the product of $3n - 6$ different terms of the type $(1 - e^{-h\nu_i/kT})^{-1}$. If any of the normal modes of vibration are degenerate, then the corresponding terms will be identical, since the frequencies are equal. A linear polyatomic molecule has $3n - 5$ vibrational modes, and hence the partition function will be the product of this number of terms.

As a general rule, the contribution of each vibrational mode to the total partition function is not greatly different from unity at moderate and low temperatures. For approximate purposes, therefore, an error in the assignment of frequencies to the vibrational modes is not serious. Most molecular vibration frequencies are greater than 500 cm^{-1} ; at ordinary temperatures (300° K) the corresponding factors in the vibrational partition function are closer to unity than 1.09. At lower temperatures and for higher frequencies, the contribution would approximate more nearly to unity. At elevated temperatures and for low frequencies, the vibrational partition function may be replaced by the classical value $kT/h\nu$ for each mode. Of the $3n - 6$ vibrational modes, $n - 1$ are stretching (valence) vibrations, and these generally have frequencies higher than 1000 cm^{-1} ; the remaining $2n - 5$ bending (deformation) vibrations usually have lower frequencies. Even if the normal frequencies of a particular molecule were not available, an approximate estimate could thus be made of the vibrational partition function from general considerations.

Attention must be called to the fact that so far in the discussion of the vibrational partition function, it has been tacitly assumed that the molecule does not contain any groups capable of internal rotation. If there are such groups, the number of vibrational modes is reduced accordingly. The problem of free internal rotation involves some complications in actual practice, and so the treatment of this subject will be deferred for the present.

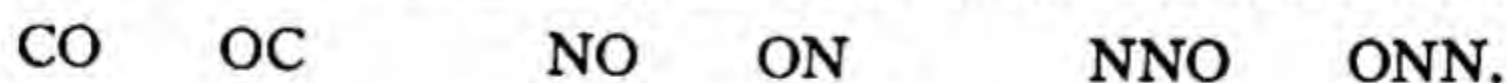
Since the vibrational partition function is the product of a number of terms, its logarithm will be the sum of the logarithms of these terms. It has been already pointed out that all the expressions for thermodynamic functions in terms of the partition function involve the logarithm of the latter and its temperature coefficient. It follows, therefore, that the contribution of each vibrational mode can be made by means of the appropriate one of the equations (60.4), (60.5) and (60.6). The sum of the resulting $3n - 6$ (or $3n - 5$, for a linear molecule) quantities gives the total vibrational contribution to the particular thermodynamic property. The calculations are greatly facilitated by the use of the tabulated Einstein functions.

APPLICATIONS OF PARTITION FUNCTIONS

63a. Entropy.—One of the important applications of partition functions is to the calculation of the entropy of gases; if the necessary spectroscopic data are available, so that the partition function and its temperature coefficient can be evaluated, the entropy can be determined with a considerable degree of accuracy. Even when the spectroscopic information is not avail-

able, surprisingly good results can be obtained by the use of the more approximate methods described above, provided the moments of inertia, or the dimensions, of the molecule and its normal vibration frequencies are known. The entropies, and other thermodynamic properties, derived from partition functions are based on the supposition of ideal behavior of the gas concerned, and so it is necessary to apply a correction to give the values of these properties for the actual gas. For this purpose the appropriate equation of state is required, and that of Berthelot has been found to be particularly convenient.

The entropies of a number of gases have been calculated from the partition functions and the results compared with the values obtained from thermal (specific heat) measurements, based on the assumption of the third law of thermodynamics that the entropy of the solid is zero at the absolute zero. In the great majority of cases studied, the agreement between the third law and statistical entropies, exclusive of the nuclear spin contribution, is excellent, thus providing support for the general accuracy of the postulate of zero entropy in the solid at 0°K . There are, however, a few substances exhibiting exceptional behavior; apart from molecules, such as ethane, methyl alcohol, etc., in which there is a possibility of free rotation, to be considered shortly, the abnormal results are obtained with hydrogen, water, carbon monoxide, nitric oxide and nitrous oxide. For the three latter compounds the thermal (third law) entropy is about 1.1 cal./deg./mole smaller than the spectroscopic (statistical) value in each case. This result suggests that the entropy of the respective solids at 0°K is not zero, as has been supposed, but that it is about 1.1 cal./deg./mole. It will be seen in Section 67c that the third law of thermodynamics can be expected to hold, i.e., the entropy of the solid is zero at 0°K , only if there is no degeneracy in the solid at low temperatures. It is possible, in the cases under consideration, that because of the similarity of the two ends of the respective molecules, the crystal lattice is unable to distinguish between the alternative arrangements



Instead of all the molecules being oriented in one direction in the crystal, two alternative orientations are thus equally probable. In other words, there is a degeneracy of two, since there are two states corresponding to the same energy. The entropy of the solid at 0°K will thus be $R \ln 2$, i.e., 1.38, instead of zero. The observed discrepancy of 1.1 cal./deg./mole shows that the arrangement in the solid of the two molecular orientations is not completely random.

The difference between thermal and spectroscopic entropies of water vapor can be accounted for by random orientation in a somewhat analogous manner, although the situation is complicated by the distribution of hydrogen bonds in the ice crystal, and also by other possibilities. The hydrogen molecule, however, presents a case of special interest, and a complete understanding of this requires a consideration of the ortho-para equilibrium.

63b. Ortho- and Para-Hydrogen.⁷—As already noted, the para state of molecular hydrogen is associated with the even values of the rotational quantum number J , whereas the ortho state is associated with the odd levels. According to the distribution law, in the classical limit, the number of molecules n_i in the i th rotational level with energy ϵ_i is given by

$$n_i = \frac{g_i}{B} e^{-\epsilon_i/kT}, \quad (63.1)$$

where g_i is the statistical weight of the particular level. In the para states the complete statistical weight of any rotational level, as seen earlier, is $i(2i+1)(2J+1)$, whereas that of the levels in the ortho states is $(i+1)(2i+1)(2J+1)$. It follows, therefore, that the ratio of the number of hydrogen molecules in the para form to that in the ortho form is

$$\frac{\text{Para-H}_2}{\text{Ortho-H}_2} = \frac{i(2i+1) \sum_{J=0,2,4,\dots} (2J+1)e^{-\epsilon_J/kT}}{(i+1)(2i+1) \sum_{J=1,3,5,\dots} (2J+1)e^{-\epsilon_J/kT}}. \quad (63.2)$$

Since the nuclear spin i for hydrogen is $\frac{1}{2}$, it follows that

$$\frac{\text{Para-H}_2}{\text{Ortho-H}_2} = \frac{1 + 5e^{-\epsilon_2/kT} + 9e^{-\epsilon_4/kT} + 13e^{-\epsilon_6/kT} + \dots}{3(3e^{-\epsilon_1/kT} + 7e^{-\epsilon_3/kT} + 11e^{-\epsilon_5/kT} + \dots)}. \quad (63.3)$$

The ratio of para- to ortho-hydrogen can be evaluated from equation (63.3) by inserting the rotational energies of the various levels as determined from the spectrum of molecular hydrogen. The terms in both numerator and denominator are summed as long as they contribute appreciably to the total at a series of temperatures. Actually $e^{-\epsilon_J/kT}$ falls off rapidly as J increases, especially at fairly low temperatures; hence, the number of terms that must be included in the summation is not large. The results obtained in this manner are recorded in Table XIX, which gives the calculated per-

TABLE XIX. EQUILIBRIUM PROPORTIONS OF PARA- AND ORTHO-HYDROGEN

Temp.	Para-H ₂	Ortho-H ₂	Temp.	Para-H ₂	Ortho-H ₂
20° K	99.82%	0.18%	120° K	32.87%	67.13%
40°	88.61	11.39	170°	27.99	72.01
60°	65.39	34.61	230°	25.42	74.58
80°	48.39	51.61	273°	25.13	74.87
100°	38.51	61.49	∞	25.00	75.00

centages of para and ortho forms of hydrogen at various temperatures. It is seen that at low temperatures hydrogen, at equilibrium, consists almost exclusively of the para form; this is because nearly all the molecules are then in the lowest ($J=0$) rotational level, and this being an even level must be a para state. As the temperature is raised, higher rotational levels are occupied to an increasing extent, and hence molecules in the ortho form are present at equilibrium. At high temperatures a limiting ratio of three parts

⁷ Dennison, *Proc. Roy. Soc., A*, 115, 483 (1927); Giauque, *J. Am. Chem. Soc.*, 52, 4808, 4816 (1930); Farkas, "Orthohydrogen, Parahydrogen and Heavy Hydrogen."

of orthohydrogen to one of parahydrogen is obtained (cf. Section 31e). This limiting value is equal to $(i + 1)/i$ (cf. Section 31e), since the two summations in equation (63.2) become identical when the temperature is sufficiently large [cf. equation (59.14)].

For ordinary hydrogen the limiting ortho-para (equilibrium) ratio is reached at about 273°K ; hence, above this temperature the effect of the nuclear spin factor has become virtually constant, and so it can be omitted from the partition function. Below 273°K , however, the nuclear spin multiplicity affects the ortho-para ratio and it must always be included in all calculations.

63c. Entropy of Molecular Hydrogen.—When the entropy of molecular hydrogen is calculated from spectroscopic data, using the complete rotational partition function given by equation (59.12), the value at 298.1°K is found to be $33.98 \text{ cal./deg./mole}$. This result is based on the tacit assumption, implied in the use of the proper partition function, that ortho-para equilibrium is always attained. The experimental (thermal) entropy of molecular hydrogen at 298.1°K is $29.64 \text{ cal./deg./mole}$, so that there is a discrepancy of 4.34 units. Since the spectroscopic value includes the nuclear spin contribution, a difference of $R \ln (2i + 1)^2$, i.e., $R \ln 4 = 2.75 \text{ cal./deg./mole}$ might have been anticipated, but the actual discrepancy, which is much larger than this, has been explained in the following manner. Owing to the difficulty of reversing nuclear spins, the ortho-para equilibrium in hydrogen is not established continuously as the gas is cooled. As a result, solid hydrogen at low temperatures, e.g., 10°K , which should consist almost exclusively of the para ($J = 0$) form, is actually made up of one part of parahydrogen to three parts of orthohydrogen. The former molecules are all in the rotationless $J = 0$ level, but the latter will be in the $J = 1$ level, and hence must still rotate in the solid. The statistical weights of these forms is $i(2i + 1)(2J + 1)$, i.e., 1 , for the para, and $(i + 1)(2i + 1)(2J + 1)$ i.e., 9 , for the ortho; hence the solid consists of one-fourth of parahydrogen of one kind, and three-fourths of orthohydrogen divided equally between nine kinds. Each of the latter must, therefore, represent one-twelfth of the total, whereas the former is one-fourth; the entropy of mixing of the ten molecular species (mole fraction x_i) is, therefore, given by

$$\begin{aligned}\Delta S &= -R \sum_i x_i \ln x_i \\ &= -R \left\{ \frac{1}{4} \ln \frac{1}{4} + 9 \left(\frac{1}{12} \ln \frac{1}{12} \right) \right\} \\ &= 4.39 \text{ cal./deg./mole.}\end{aligned}$$

This is the entropy the experimental solid would have at 0°K , instead of the value of $R \ln 4$ which it would have had if ortho-para equilibrium had been established; in the latter event all the molecules would have been in the rotationless ($J = 0$) para state. In order to obtain the thermal entropy, therefore, it is necessary to subtract 4.39 from the statistical value of 33.98 , giving $29.59 \text{ cal./deg./mole}$, in excellent agreement with that observed.

However, if the entropy of molecular hydrogen is to be used in conjunction with thermal entropies of other substances, the nuclear spin entropy $R \ln 4$, i.e., 2.75, should be subtracted from 33.98, giving a value for the virtual (or practical) entropy of 31.23 cal./deg./mole at 298.1° K.

A discrepancy analogous to that just described has been observed between the spectroscopic and thermal entropies of molecular deuterium. It can be explained in a manner similar to that for the lighter isotope.

63d. Heat Capacities.—Partition functions have also been applied to the calculation of heat capacities, by utilizing the equations derived in Section 56c. At all temperatures above the very lowest, the translational contribution to the heat capacity is the classical value $\frac{3}{2}R$, and so it is sufficient to consider the electronic, rotational and vibrational contributions only. Since the heat capacity depends on the second derivative of the partition function with respect to temperature, or to $1/T$, as seen from equations (56.20) to (56.22), it is evident that the value of the partition function must be known accurately. At sufficiently high temperatures the rotational heat capacity becomes equal to $\frac{1}{2}R$ for each rotational degree of freedom, while the contribution of every vibrational mode is R , in agreement with the classical equipartition principle. Nevertheless, it is possible for the total heat capacity derived from the partition function to exceed the classical value; this is because the latter does not take into account the effects of electron multiplicity in the ground state and of excited states.

One of the most interesting applications of heat capacity calculations from partition functions arises in connection with the ortho-para hydrogen system. At temperatures below 300° K all the molecules are in their lowest vibrational state, and so under these conditions the vibrational heat capacity is zero. Since there are no excited or multiplet states of molecular hydrogen to consider, the treatment may be restricted to the rotational contribution to the heat capacity. If the ortho-para equilibrium in hydrogen gas were always established at every temperature, the rotational partition function of the system would be given by [cf. equation (63.2)]

$$Q_r = \sum_{J=0, 2, 4, \dots} (2J + 1)e^{-J(J+1)/kT} + 3 \sum_{J=1, 3, 5, \dots} (2J + 1)e^{-J(J+1)/kT} \quad (63.4)$$

since the nuclear spin i of the hydrogen atom is $\frac{1}{2}$. The first term in this expression is for the para form, and the second is that for the ortho form.

Since the rotational energy levels of the hydrogen molecule are known with considerable accuracy, from the band spectrum of this substance, the partition function, and hence the rotational heat capacity, can be calculated at various temperatures. When the results obtained in this manner were compared with the observed values, marked differences were found at temperatures below about 270° K. The explanation of the discrepancies lay in the fact that the experimental heat capacity determinations were made with hydrogen in which ortho-para equilibrium had not been established at every temperature, for the reason given in the preceding section.

The gas used actually consisted of a mixture of three parts of orthohydrogen and one part of parahydrogen. The heat capacity of such a system can be calculated by considering the ortho and para forms as separate gases, whose rotational partition functions are

$$Q_{\text{para}} = \sum_{J=0, 2, 4, \dots} (2J + 1)e^{-\epsilon J/kT} \quad (63.5)$$

and

$$Q_{\text{ortho}} = 3 \sum_{J=1, 3, 5, \dots} (2J + 1)e^{-\epsilon J/kT} \quad (63.6)$$

respectively. From these the separate rotational heat capacities, C_{para} and C_{ortho} can be calculated, and the experimental values will then be given by the expression

$$C_r = \frac{1}{4}C_{\text{para}} + \frac{3}{4}C_{\text{ortho}}.$$

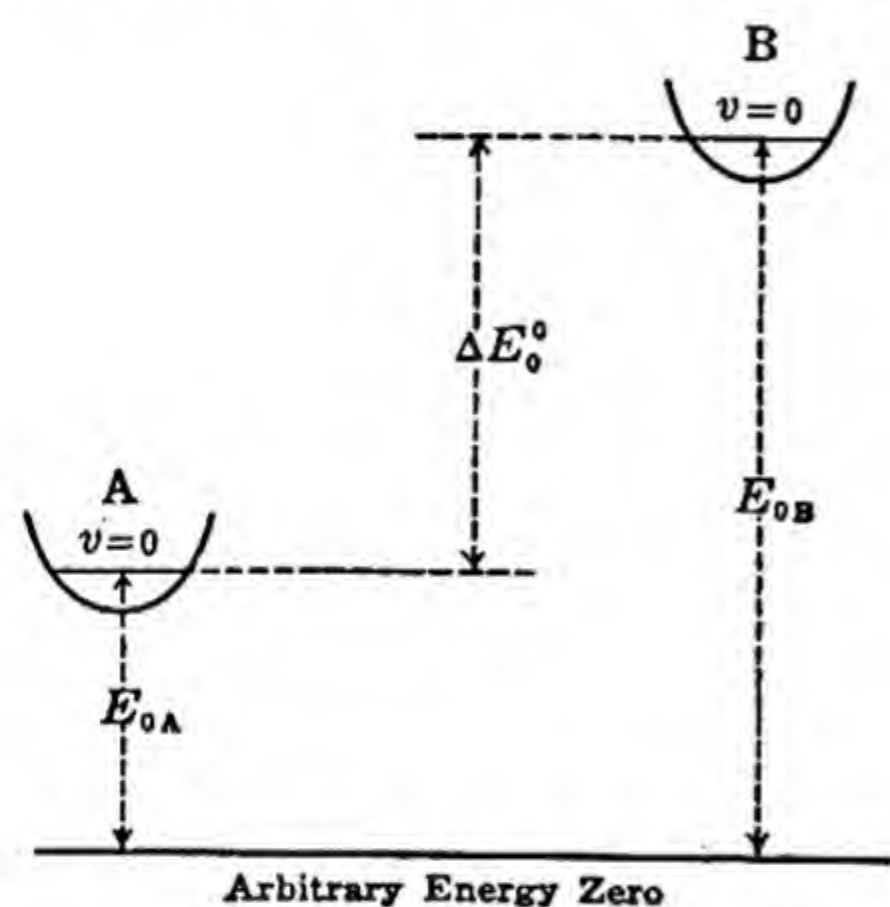


FIG. 42. Change of energy zero

The results obtained in this manner were found to be in excellent agreement with the experimental heat capacities at all temperatures down to about 60° K. It may be noted that pure parahydrogen has been prepared and its heat capacity determined over the temperature range from about 80° to 300° K. The values are very close to those derived by the use of equation (63.5).

64a. Free Energy and Equilibria in Gaseous Systems.—

The free energy of a mole of an ideal gas can be related to the partition function by means of equation (56.9); since the methods of deriving partition functions for various types of molecules are available, at least in principle, it should be possible to calculate the free energies of the substances taking part in a reaction. The free energy change ΔF^0 , for reactants and products in their standard states, is related to the equilibrium constant K of the reaction by the equation

$$-\Delta F^0 = RT \ln K. \quad (64.1)$$

Hence there should be a close connection between the partition functions of the substances involved in the reaction and the equilibrium constant of the system.

It was seen in Section 56e that the choice of the energy zero for the evaluation of the partition function of a given molecule has no effect on the heat capacity and entropy, but it introduces an additive term in the expressions for the total energy and free energy. In the treatment of previous sections the convention has been adopted of taking the energy zero for each

molecular species at its own zero-point ($v = 0$, $J = 0$) level. However, when it is required to calculate the change of free energy of a reaction, it is necessary to refer the energies of all the substances to one and the same, arbitrary, zero level. If the energy difference between the arbitrary zero from which all energies are to be reckoned and the zero-point level of a particular molecular species is represented by E_0 per mole, (Fig. 42), then according to equation (56.36)

$$Q_{E_0} = e^{-E_0/RT} Q, \quad (64.2)$$

where Q_{E_0} is the partition function based on the new energy zero, while Q is the value used in earlier parts of this chapter. It should be noted that E_0 is the energy per mole, instead of per molecule; for this reason RT is used in the exponent instead of the familiar kT . If the new expression for the partition function is inserted into equation (56.9), the free energy per mole, based on the new energy zero, becomes

$$F = -RT \ln \frac{Q_{E_0}}{N}, \quad (64.3)$$

and consequently, by equation (64.2),

$$F = -RT \ln \frac{Q}{N} + E_0. \quad (64.4)$$

For the evaluation of equilibrium constants, it is necessary to consider the free energy changes when the substances are in their standard states; using the superscript zero, in the usual manner to represent the standard state, it follows that

$$F^0 = -RT \ln \frac{Q^0}{N} + E_0^0, \quad (64.5)$$

the partition function Q^0 being now for the given species in its standard state. For gases, and it is only to ideal gas systems that the partition function concept as developed in this chapter is applicable, the standard state is chosen as the ideal gas at 1 atm. pressure. This choice does not affect any of the contributions to the partition function associated with internal degrees of freedom, since these are all independent of the volume or pressure of the system. The only contribution that has to be considered is that due to the translational degrees of freedom; this may be written in the form of equation (57.6), viz.,

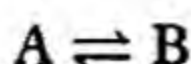
$$Q_t = \frac{(2\pi mkT)^{3/2}}{h^3} \cdot \frac{RT}{P},$$

and hence for the standard state of 1 atm., this becomes

$$Q_t^0 = \frac{(2\pi mkT)^{3/2}}{h^3} RT, \quad (64.6)$$

where R is expressed in cc.-atm. per degree units.

64b. Partition Functions and Equilibrium Constant.—Consider the simple reaction



involving ideal gases; the standard free energy per mole of the reactant A is

$$F_A^0 = -RT \ln \frac{Q_A^0}{N} + E_{0A}^0,$$

while for a mole of product B,

$$F_B^0 = -RT \ln \frac{Q_B^0}{N} + E_{0B}^0.$$

The standard free energy decrease $-\Delta F^0$ for the reaction is then

$$-\Delta F^0 = F_A^0 - F_B^0 = -RT \ln \frac{(Q^0/N)_A}{(Q^0/N)_B} - \Delta E_0^0, \quad (64.7)$$

where ΔE_0^0 is given by

$$\Delta E_0^0 = E_{0B}^0 - E_{0A}^0. \quad (64.8)$$

As seen in Fig. 42, ΔE_0^0 is the difference in energy between the zero-point levels of the product A and the reactant B; in other words, ΔE_0^0 is the energy change in the reaction calculated for the absolute zero of temperature, i.e., when all the molecules are in their lowest (zero-point) vibrational and rotational states. Making use of equation (64.1) in the form

$$-\Delta F^0 = RT \ln K_p,$$

since the standard state is 1 atm., it follows from equation (64.8) that

$$\begin{aligned} RT \ln K_p &= RT \ln \frac{(Q^0/N)_B}{(Q^0/N)_A} - \Delta E_0^0, \\ \therefore K_p &= \frac{(Q^0/N)_B}{(Q^0/N)_A} e^{-\Delta E_0^0/RT}, \end{aligned} \quad (64.9)$$

where the partition functions Q^0 refer to 1 atm. pressure.

It is obvious that equation (64.9) is of fundamental importance, for it gives a direct connection between the equilibrium constant of an ideal gas reaction and the partition functions of the reacting substances and products. This expression can be readily extended to cover the case of a reaction of greater complexity; thus, for the general reaction

$$\begin{aligned} aA + bB + \cdots &\rightleftharpoons lL + mM + \cdots, \\ K_p &= \frac{(Q^0/N)_L^l (Q^0/N)_M^m \cdots}{(Q^0/N)_A^a (Q^0/N)_B^b \cdots} e^{-\Delta E_0^0/RT}. \end{aligned} \quad (64.10)$$

As before, the partition functions refer to the standard state of 1 atm. pressure, and ΔE_0^0 is the standard change in the (total) energy of the reaction at 0° K.

64c. Free Energy Functions.—For convenience in calculating equilibrium constants, it has become the practice to tabulate values of the function $-(F^0 - E_0^0)/T$ for various substances, rather than the partition function itself. It can be seen from equation (64.5) that

$$-\frac{(F^0 - E_0^0)}{T} = R \ln \frac{Q^0}{N}, \quad (64.11)$$

and hence the left-hand side, sometimes called the *free energy function*, can be readily obtained from the partition function. It will be recalled that Q^0 is the ordinary partition function, as calculated in earlier sections of this chapter, based on the zero-point level of the molecule itself as the energy zero. Hence, the methods whereby it can be derived may be regarded as known; the only change necessary is that equation (64.6) should be used for the translational partition function, because of the postulated standard state, viz., 1 atm.

The change in the free energy function accompanying a particular reaction can be readily obtained from the tabulated data for various substances at a series of temperatures. In order to calculate the equilibrium constant, use is made of the following equations

$$\begin{aligned} -\Delta \left(\frac{F^0 - E_0^0}{T} \right) &= -\frac{\Delta F^0}{T} + \frac{\Delta E_0^0}{T} \\ &= R \ln K_p + \frac{\Delta E_0^0}{T}, \end{aligned}$$

or

$$R \ln K_p = -\Delta \left(\frac{F^0 - E_0^0}{T} \right) - \frac{\Delta E_0^0}{T}, \quad (64.12)$$

so that from a knowledge of the $-(F^0 - E_0^0)/T$ functions, or of the partition functions, of reactants and products of a chemical reaction, it is possible to calculate the equilibrium constant, provided ΔE_0^0 for the process is known.

64d. Evaluation of ΔE_0^0 .—Several methods are available for obtaining ΔE_0^0 ; by definition

$$H = E + PV, \quad (64.13)$$

and for one mole of an ideal gas $H = E + RT$, or in the standard state

$$H^0 = E^0 + RT.$$

For the standard change in the heat content of a reaction,

$$\Delta H^0 = \Delta E^0 + \Delta n(RT), \quad (64.14)$$

where Δn is the increase in the number of molecules in the reaction. At the absolute zero of temperature, i.e., T is 0°K , equation (64.14) becomes

$$\Delta H_0^0 = \Delta E_0^0. \quad (64.15)$$

If the heat of reaction at constant pressure, with reactants and products in their standard states, i.e., ΔH^0 , at a definite temperature is known, and if the heat contents of reactants and products are available, ΔH^0 can be derived from the familiar form of the Kirchhoff equation, viz.,

$$\Delta H^0 = \Delta H_0^0 + \int_0^T \Delta C_P dT. \quad (64.16)$$

If ΔC_P can be represented as a function of temperature,

$$\Delta C_P = \alpha + \beta T + \gamma T^2 + \dots,$$

and since ΔH_0^0 is equal to ΔE_0^0 , by equation (64.15), then equation (64.16) becomes

$$\Delta H^0 = \Delta E_0^0 + \alpha T + \frac{1}{2}\beta T^2 + \frac{1}{3}\gamma T^3 + \dots \quad (64.17)$$

It is evident that ΔE_0^0 may be calculated if, in addition to the change in heat content ΔH^0 of the reaction, the heat capacities of reactants and products are known as functions of the temperature.

A second procedure for evaluating ΔE_0^0 from ΔH^0 does not require a knowledge of heat capacities, but it derives these, indirectly, from the partition functions. Subtracting the quantity E_0^0 from both sides of equation (64.13), the result is

$$H^0 - E_0^0 = (E^0 - E_0^0) + RT. \quad (64.18)$$

The energy E^0 , based on the arbitrary zero, as described in Section 64a, is obtained by utilizing the familiar equation for the energy in terms of the partition function, where the latter is now $Q_{E_0}^0$, i.e., Q_{E_0} in the standard state; thus

$$E^0 = RT^2 \left(\frac{\partial \ln Q_{E_0}^0}{\partial T} \right)_V. \quad (64.19)$$

Introducing equation (64.2) so as to eliminate Q_{E_0} and replace it by the more usual function Q , equation (64.19) becomes

$$E^0 - E_0^0 = RT^2 \left(\frac{\partial \ln Q^0}{\partial T} \right)_V. \quad (64.20)$$

Combination of equations (64.18) and (64.20) now gives

$$H^0 - E_0^0 = RT^2 \left(\frac{\partial \ln Q^0}{\partial T} \right)_V + RT \quad (64.21)$$

$$= RT^2 \left(\frac{\partial \ln Q^0}{\partial T} \right)_P. \quad (64.22)$$

The values of $H^0 - E_0^0$ for various substances, derived from the partition function by means of equation (64.22), have been tabulated, so that $\Delta(H^0 - E_0^0)$ for a reaction can be readily determined. From this datum,

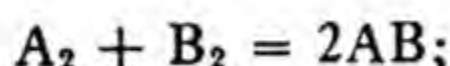
together with the known change in the heat content ΔH^0 of the reaction, it is possible to evaluate ΔE_0^0 ; thus, since

$$\Delta(H^0 - E_0^0) = \Delta H^0 - \Delta E_0^0,$$

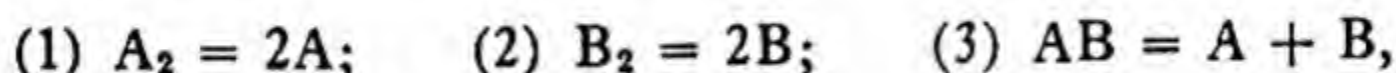
it follows that

$$\Delta E_0^0 = \Delta H^0 - \Delta(H^0 - E_0^0).$$

A third method for obtaining ΔE_0^0 that can be employed in certain instances is to make use of spectroscopic data for the heats of dissociation (cf. Section 32d); these are the ΔE_0^0 values for the respective reactions. Suppose it is required to determine ΔE_0^0 for the reaction



then the spectroscopic heats of dissociation of the three reactions,



must be known. If these are D_1 , D_2 and D_3 , respectively, reckoned from the zero-point level in each case, then the required ΔE_0^0 is $D_1 + D_2 - 2D_3$.

64e. Entropies and Entropy Changes in Chemical Reactions.—It is of interest to call attention to the fact that the tabulated data for $-(F^0 - E_0^0)/T$ and for $(H^0 - E_0^0)/T$ can be utilized directly to derive the entropy of a substance or of the entropy changes in a reaction, at any temperature. Since $F = H - TS$, it follows that, for the standard state,

$$\begin{aligned} S^0 &= \frac{H^0 - F^0}{T} \\ &= \frac{H^0 - E_0^0}{T} - \frac{F^0 - E_0^0}{T}. \end{aligned} \quad (64.23)$$

If the entropy change of a process is required, the values of $\Delta(H^0 - E_0^0)/T$ and $-\Delta(F^0 - E_0^0)/T$ can be obtained from the tables for the substances involved in the given reaction.

64f. Equilibrium Constant in Terms of Concentrations.—Although the standard state for a gas is generally taken as the ideal gas at 1 atm. pressure, so that the equilibrium constant is obtained in terms of partial pressures expressed in atmospheres, it is sometimes desirable to make use of an alternative standard state, namely, the ideal gas at unit concentration. A simple (hypothetical) form of such unit concentration would be 1 mole per cc., and with this standard state the equilibrium constant K_c is determined by the expression,

$$-\Delta F^0 = RT \ln K_c,$$

in terms of the same concentration unit. The relationship between K_c and the partition functions for a general reaction is thus given by an equation of

the same form as (64.10), that is,

$$K_c = \frac{(Q_c^0/N)_L (Q_c^0/N)_M \cdots}{(Q_c^0/N)_A (Q_c^0/N)_B \cdots} e^{-\Delta E_0^0/RT}. \quad (64.24)$$

The subscript c , as applied to the symbol Q_c^0 for the partition function in the standard state, is meant to indicate that the standard state is here unit concentration; the problem now arises as to how Q_c^0 differs from the partition functions Q^0 employed previously. As before, all contributions other than that for the translational degrees of freedom are unaffected; the latter is now employed in the form

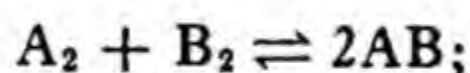
$$Q_t = \frac{(2\pi mkT)^{3/2}}{h^3} V,$$

and if the standard state is 1 mole per cc., V is unity, and so

$$Q_t^0 = \frac{(2\pi mkT)^{3/2}}{h^3}. \quad (64.25)$$

This is the value of the translational partition function to be used in the calculation of Q_c^0 .

64g. Effect of Nuclear Spin.—It was mentioned earlier that the omission of the nuclear spin factor does not affect the value of the free energy change in a reaction provided, of course, there is no change in ortho-para ratios. This can be shown more explicitly by means of the equation derived above for the equilibrium constants. Consider the simple reaction



the equilibrium constant is here independent of the chosen standard state, because there is no change in the number of molecules in the reaction, and it is given by

$$K = \frac{(Q^0/N)_{AB}^2}{(Q^0/N)_{A_2} (Q^0/N)_{B_2}} e^{-\Delta E_0^0/RT}. \quad (64.26)$$

Suppose that from the complete partition function the nuclear spin factor, which is $2i + 1$ for every atom, is extracted, leaving a residual contribution Q' for all other degrees of freedom; i.e.,

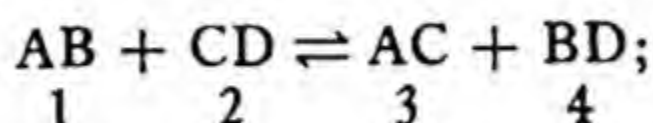
$$Q^0 = Q' \prod_i (2i + 1).$$

Then equation (64.26) would become

$$\begin{aligned} K &= \frac{\{(2i_A + 1)(2i_B + 1)(Q'/N)_{AB}\}^2}{\{(2i_A + 1)^2(Q'/N)_{A_2}\} \{(2i_B + 1)^2(Q'/N)_{B_2}\}} e^{-\Delta E_0^0/RT} \\ &= \frac{(Q'/N)_{AB}^2}{(Q'/N)_{A_2} (Q'/N)_{B_2}} e^{-\Delta E_0^0/RT}, \end{aligned}$$

which is exactly of the same form as equation (64.26), the partition functions Q^0 being replaced by Q' . It follows, therefore, that in calculating the equilibrium constant of a reaction, the nuclear spin factors may be omitted from the partition function; the symmetry number must, of course, always be retained. It should be understood that this rule does not apply for reactions involving ortho-para changes (cf. Section 63b).

64h. Isomolecular Reactions.—When there is no change in the number of molecules as the result of a reaction, a very simple, if somewhat approximate, expression can be derived for the equilibrium constant, particularly if diatomic molecules only are involved. Consider, for example, the reaction



the equilibrium constant, independent of standard state, is given by

$$K = \frac{(Q_3/N)(Q_4/N)}{(Q_1/N)(Q_2/N)} e^{-\Delta E_0^0/RT} \quad (64.28)$$

where, for simplicity, the symbols Q_1 , Q_2 , Q_3 and Q_4 are used to represent the partition functions of the diatomic molecules AB, CD, AC and BD, respectively, in their standard states. As there is no change in the number of molecules in the reaction, it follows that

$$K = \frac{Q_3 Q_4}{Q_1 Q_2} e^{-\Delta E_0^0/RT}. \quad (64.29)$$

Since the nuclear spin factor may be ignored, and the electronic statistical weight may be taken as unity, it is possible to write, in general,

$$Q = Q_t Q_v Q_r. \quad (64.30)$$

The expression for Q_t , the translational partition function, is

$$\begin{aligned} Q_t &= \frac{(2\pi mkT)^{3/2}}{h^3} V \\ &= aM^{3/2}, \end{aligned} \quad (64.31)$$

where M is the molecular weight, and a is a constant, at definite temperature and volume, that is independent of the nature of the substance. In a similar manner, the equation for the **rotational** partition function may be put in a simplified form; thus,

$$\begin{aligned} Q_r &= \frac{8\pi^2 I k T}{\sigma h^2} \\ &= b \frac{I}{\sigma}, \end{aligned} \quad (64.32)$$

where b is also independent of the substance, at constant temperature. Making the reasonable approximation that the contribution of the vibrational terms is unity, and utilizing equations (64.30), (64.31) and (64.32), equation (64.29) becomes

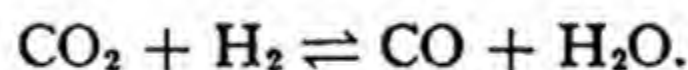
$$K = \left(\frac{M_3 M_4}{M_1 M_2} \right)^{3/2} \frac{I_3 I_4}{I_1 I_2} \cdot \frac{\sigma_1 \sigma_2}{\sigma_3 \sigma_4} e^{-\Delta E_0^0 / RT},$$

or

$$\ln K = -\frac{\Delta E_0^0}{RT} + \frac{3}{2} \ln \frac{M_3 M_4}{M_1 M_2} + \ln \frac{I_3 I_4}{I_1 I_2} + \ln \frac{\sigma_1 \sigma_2}{\sigma_3 \sigma_4}. \quad (64.33)$$

The value of the equilibrium constant may thus be derived from a knowledge of ΔE_0^0 for the reaction, and of the molecular weights, moments of inertia, and symmetry numbers of the reactants and products. Equations of the type of (64.33) have been employed particularly in the study of isotopic exchange reactions, where the error due to the cancellation of the vibrational partition functions is very small, especially if the temperature is not too high.⁸

64i. Calculation of Equilibrium Constants and Free Energies.—The most convenient and accurate method for employing partition functions for the calculation of free energies and equilibrium constants is to utilize the tables of free energy functions obtained from spectroscopic data, when they are available. An interesting case, for which all the necessary quantities have been calculated, is the so-called "water gas" reaction,



The free energy functions $-(F^0 - E_0^0)/T$ for reactants and products at 1000° K, excluding the nuclear spin contribution in every case, are as follows:

	CO ₂	H ₂	CO	H ₂ O
$-(F^0 - E_0^0)/T$	54.137	32.752	48.876	46.999
$\therefore -\frac{\Delta(F^0 - E_0^0)}{T}$	= 8.986 cal./deg./mole at 1000° K.			

By means of the methods described in Section 64d, the value of ΔE_0^0 for the reaction is found to be 9,640 cal., and hence

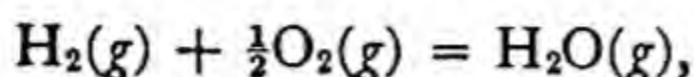
$$-\frac{\Delta F^0}{T} = R \ln K = -0.654$$

$$\therefore K = 0.719.$$

The extrapolated experimental value at 1000° K, which is probably less accurate than that just calculated from spectroscopic data, is 0.71.

⁸ Urey and Rittenberg, *J. Chem. Phys.*, 1, 137 (1933); Urey and Greiff, *J. Am. Chem. Soc.*, 57, 321 (1935).

Another important datum that can be derived from tabulated free energy functions is the free energy of formation of water, that is, of the reaction



at 25°; this is utilized in the calculation of the standard E.M.F. of the hydrogen-oxygen cell and of the standard potential of the oxygen electrode. From the tables the following results, from which nuclear spin effects have again been excluded, are obtained at 298.16° K:

	H_2	$\frac{1}{2}\text{O}_2$	$\text{H}_2\text{O}(g)$
$-(F^0 - E_0^0)/T$	24.436	21.041	37.179

$$\therefore -\frac{\Delta(F^0 - E_0^0)}{T} = -8.297 \text{ cal./deg./mole at } 298.16^\circ \text{ K.}$$

The value of ΔE_0^0 for the reaction is found to be $-57,120$; hence,

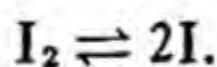
$$-\frac{\Delta F^0}{T} = -8.297 + \frac{57,120}{T}$$

$$\therefore \Delta F^0 = 298.16(8.297) - 57,120$$

$$= -54,650 \text{ cal. at } 298.16^\circ \text{ K.}$$

This value is in good agreement with the best experimental data.

When the free energy functions are not available, surprisingly good results may be obtained, particularly at fairly high temperatures, by the use of the approximate expressions for the partition functions, e.g., equation (61.3) for a diatomic molecule. The procedure may be illustrated by reference to calculation of the equilibrium constant for the dissociation of molecular iodine into atoms, viz.,



According to equation (64.9), it is seen that

$$K_p = \frac{(Q^0/N)_1^2}{(Q^0/N)_2} e^{-\Delta E_0^0/RT},$$

where the subscripts 1 and 2 refer to the atoms and molecules, respectively. Hence, by means of the results already derived,

$$K_p = \frac{\left\{ g_1 \frac{(2\pi m_1 k T)^{3/2}}{h^3} \cdot \frac{RT}{N} \right\}^2}{g_2 \frac{(2\pi m_2 k T)^{3/2}}{h^3} \cdot \frac{RT}{N} \cdot \frac{8\pi^2 I k T}{\sigma h^2} (1 - e^{-hc\omega/kT})^{-1}} e^{-\Delta E_0^0/RT}, \quad (64.34)$$

where g_1 and g_2 are the electronic statistical weights; the nuclear spin factors have been omitted in each case. Except at very high temperature, all the iodine atoms may be presumed to be in the lowest, i.e., $^2P_{3/2}$, state;

hence j is $\frac{3}{2}$, and the electronic contribution g_1 to the partition function is $(2 \times \frac{3}{2}) + 1 = 4$. As with most molecules possessing an even number of electrons, g_2 for the iodine molecule may be taken as unity. From its electronic spectrum, the moment of inertia I of molecular iodine is known to be 742.6×10^{-40} g. cm.², and the vibration frequency ω is 213.67 cm.⁻¹. Spectroscopic data (cf. Section 32d) also show that ΔE_0^0 is 35,480 cal., and since σ is equal to 2, all the information is available for the calculation of K_p by means of equation (64.34). The results obtained in this manner by Gibson and Heitler (1928) are compared with the experimental values of Starck and Bodenstein (1910) in Table XX;⁹ the agreement is seen to be remarkably good.

TABLE XX. EQUILIBRIUM CONSTANTS FOR DISSOCIATION OF MOLECULAR IODINE

Temperature	Equilibrium Constant	
	Calculated	Observed
800° C	1.13×10^{-2}	1.14×10^{-2}
900°	4.79×10^{-2}	4.74×10^{-2}
1000°	1.65×10^{-1}	1.65×10^{-1}
1100°	4.94×10^{-1}	4.92×10^{-1}
1200°	1.22	1.23

64j. Reaction Rates.¹⁰—It was seen from the quantum mechanical calculations in Section 25a that when two molecules undergo reaction, their energy first increases to a maximum and then decreases as the products of the reaction separate. The difference between the maximum energy and that of the reactants is the activation energy of the process. The general conclusions reached in the consideration of two molecules may be extended to all chemical process. It may be supposed that in any atomic or molecular process requiring an activation energy, the atoms or molecules must first come together to form an *activated state*, or *activated complex*. These complexes may be regarded as situated at the top of the barrier, on the potential energy surface (cf. Fig. 19), lying between the initial and final states. The rate of the reaction is then given by the velocity with which the activated complexes travel over the top of the barrier from the initial to the final state. It can be shown that the configuration corresponding to the system in the activated state, i.e., at the top of the energy barrier, has all the properties of an ordinary molecule, except that one normal vibration frequency has an imaginary value. In other words, the activated complex may be regarded as possessing translational and rotational degrees of freedom like a normal molecule; in addition, it remains stable for all modes of vibration, i.e., for all atomic displacements, except one, and this one, which corresponds to motion along the reaction path on the potential energy surface, leads to decomposition. Since the activated complex must presumably retain its $3n$ degrees of freedom, where n is the number of atoms it contains, the imaginary

⁹ Cf. Perlman and Rollefson, *J. Chem. Phys.*, 9, 362 (1941).

¹⁰ Eyring, *J. Chem. Phys.*, 3, 107 (1935); for further details and applications, see Glasstone, Laidler and Eyring, "The Theory of Rate Processes."

vibration must be replaced by another degree of freedom, and this is taken to be the motion in the reaction path, i.e., in the decomposition coordinate. If the top of the energy barrier, where the activated complex is situated, is relatively flat, this degree of freedom may be treated statistically as a one-dimensional translation.

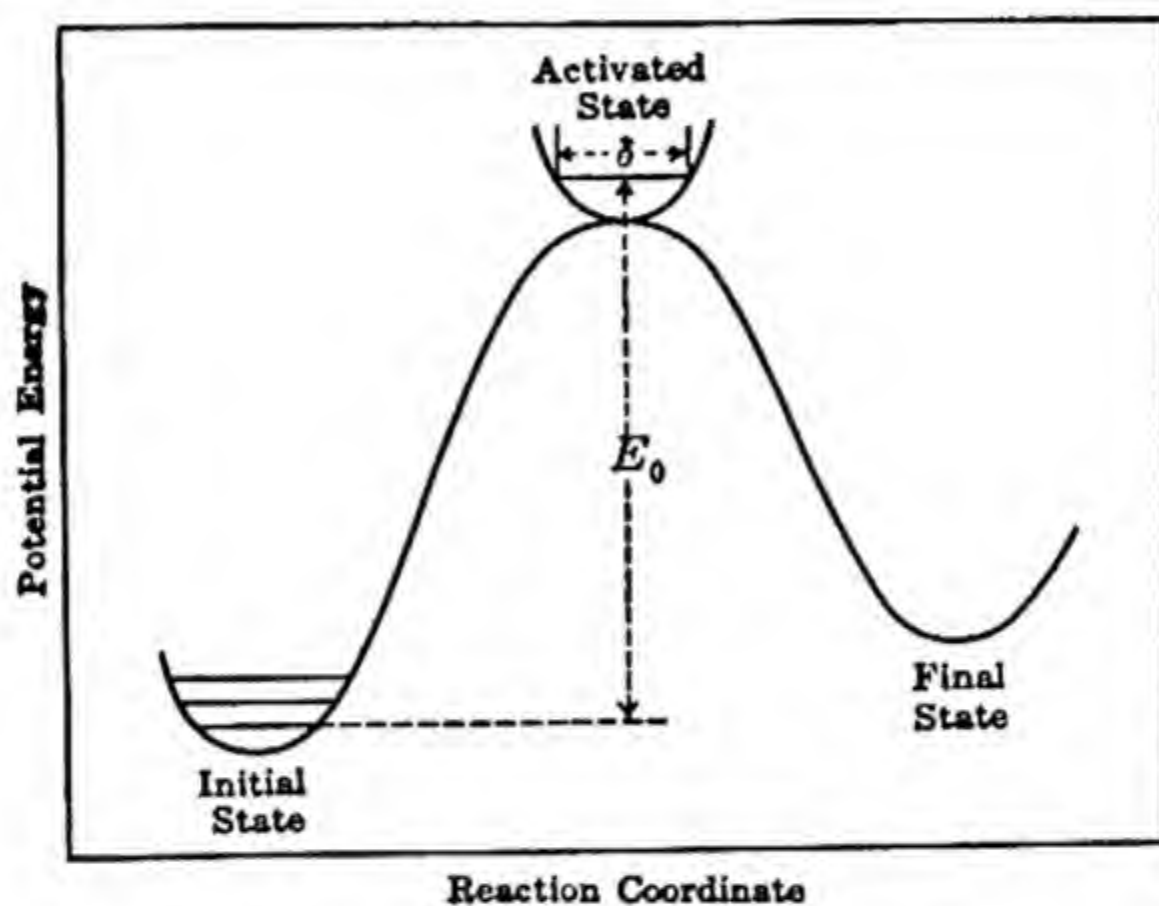


FIG. 43. Potential energy curve for chemical reaction

If the activated complexes are regarded as being always in equilibrium with the reactants, it is possible to apply the results of statistical mechanics to the former, as well as to the latter. It was seen in Section 49b that the means value \bar{x} of the component of velocity of a molecule in a particular direction is given by

$$\bar{x} = \left(\frac{kT}{2\pi m} \right)^{1/2}, \quad (64.35)$$

and consequently this may be taken as the average rate at which the activated complexes pass over the energy barrier in one direction along the coordinate of decomposition. In this equation, m is to be regarded as the effective mass of the activated complex along the coordinate of decomposition. It is now convenient to define arbitrarily an "activated state," which may be imagined to exist at the top of the energy barrier (Fig. 43) in a potential box of length δ ; as will be seen shortly, the actual length is immaterial, as it cancels out in the final expression. The average time τ for an activated complex to cross the barrier, that is, to pass through the "activated state," is thus equal to the length δ divided by the mean velocity \bar{x} ; so that

$$\tau = \frac{\delta}{\bar{x}} = \delta \left(\frac{2\pi m}{kT} \right)^{1/2}. \quad (64.36)$$

The fraction of the activated complexes crossing the barrier in unit time is $1/\tau$; hence, if c_+ is the number of activated complexes in unit volume lying

in the "activated state," the quantity c_{\ddagger}/τ gives the number of complexes crossing the barrier per unit volume in unit time. If every complex that moves across the barrier in the direction under consideration falls to pieces, then c_{\ddagger}/τ must be equal to the reaction velocity; that is,

$$\text{Rate of reaction} = \frac{c_{\ddagger}}{\tau} = c_{\ddagger} \left(\frac{kT}{2\pi m} \right)^{1/2} \frac{1}{\delta}. \quad (64.37)$$

If the substances, A, B, ..., etc., are reacting to form the activated complex, and k_r is the specific reaction rate,¹¹ using concentration units, the rate of reaction is equal to $k_r c_A c_B \dots$, where the concentration terms are expressed in molecules per unit volume. It follows, therefore, from equation (64.37), that

$$\text{Rate of reaction} = k_r c_A c_B \dots = c_{\ddagger} \left(\frac{kT}{2\pi m} \right)^{1/2} \frac{1}{\delta},$$

and hence

$$k_r = \frac{c_{\ddagger}}{c_A c_B \dots} \left(\frac{kT}{2\pi m} \right)^{1/2} \frac{1}{\delta}. \quad (64.38)$$

It was postulated above that the activated complex is in equilibrium with the reactants, and so it is possible to write the equilibrium constant for the system as

$$K_c = \frac{c_{\ddagger}}{c_A c_B \dots}, \quad (64.39)$$

the various components being assumed to behave ideally. This equilibrium constant may be written in terms of the respective partition functions by means of equation (64.25); however, since the standard state chosen here, for convenience, is that of one *molecule* (instead of one mole) in unit volume, the N 's are omitted from this equation. Consequently, it is possible to write

$$K_c = \frac{Q'_{\ddagger}}{Q_A Q_B \dots} e^{-E_0/RT}, \quad (64.40)$$

where E_0 is used, in place of ΔE_0^0 , for the energy difference per mole between the zero-point levels in the final and initial states of the equilibrium (see Fig. 42). The partition functions are the values for the standard states, the translational contribution being given by equation (64.25). By combining equations (64.38), (64.39) and (64.40), it is seen that

$$k_r = \frac{Q'_{\ddagger}}{Q_A Q_B \dots} \left(\frac{kT}{2\pi m} \right)^{1/2} \frac{1}{\delta} e^{-E_0/RT}. \quad (64.41)$$

¹¹ In order to avoid confusion between the symbol k for the specific reaction rate and that for the Boltzmann constant, which will appear in the same equations, the former is distinguished by the use of the subscript r , i.e., k_r .

The partition function of the activated complex, Q'_{\ddagger} , as used in equations (64.40) and (64.41), includes the contribution of the translational degree of freedom in the decomposition coordinate; this may, for convenience, be extracted, so that

$$Q'_{\ddagger} = Q_{t(1)} Q_{\ddagger}, \quad (64.42)$$

where $Q_{t(1)}$ represents the partition function for one degree of translational freedom, and Q_{\ddagger} is the partition function of the activated complex exclusive of this factor. According to equation (57.4), the value of $Q_{t(1)}$ in the present case is given by

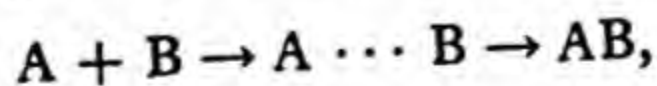
$$Q_{t(1)} = \frac{(2\pi mkT)^{1/2}}{h} \delta, \quad (64.43)$$

where δ is the postulated length of the potential box containing the "activated state." Insertion of the results of equations (64.42) and (64.43) into (64.41), then gives

$$k_r = \frac{kT}{h} \cdot \frac{Q_{\ddagger}}{Q_A Q_B \dots} e^{-E_0/RT}. \quad (64.44)$$

It should be noted that the combination of the two terms involving the properties of the activated complex along the decomposition coordinate, viz., $(2\pi mkT)^{1/2}/h$ and $(kT/2\pi m)^{1/2}$, has given the quantity kT/h , which is independent of the nature of the reactants or the reaction. It is, therefore, a universal constant, with the dimensions of a frequency, for any definite temperature; its value is practically $2 \times 10^{10} T \text{ sec.}^{-1}$. The result expressed by equation (64.44) is the basis of what has become known as the *theory of absolute reaction rates*; it provides, in principle, a method for calculating the rate of a chemical reaction. The partition functions of the reactants may be regarded as known, and the necessary information for evaluating that of the activated complex, viz., dimensions and vibration frequencies, can be derived from the potential energy surface obtained from the quantum mechanical calculations. Further, E_0 , which is the (hypothetical) activation energy of the process at the absolute zero of temperature, can also be obtained from the height of the barrier on the potential energy surface.

The complete data required for calculating the rate of a reaction are available in a few simple cases only, but even where the full information cannot be obtained, many useful conclusions can be drawn by introducing the appropriate expressions for the partition functions in equation (64.44). For this purpose it is most convenient, and sufficiently accurate, to utilize the approximate equations given in Sections 61b, 62b and 62c. As a very simple illustration, the reaction between two atoms A and B, viz.,



may be considered, where $A \dots B$ represents the activated complex. The latter will have three degrees of translational freedom and two of rotation,

just like a normal diatomic molecule; however, the one vibrational mode usually possessed by such a molecule is now absent, since it has been replaced by the contribution of the degree of freedom in the decomposition coordinate. The latter is not included in Q_{\ddagger} , as seen above, and so it follows that

$$Q_{\ddagger} = \frac{\{2\pi(m_A + m_B)kT\}^{3/2}}{h^3} \cdot \frac{8\pi^2 I kT}{h^2}, \quad (64.45)$$

where the first factor, the ordinary translational contribution, is obtained from equation (64.25) by inserting $m_A + m_B$ for the mass of the activated complex. The moment of inertia I of the complex is given by

$$I = \frac{m_A m_B}{m_A + m_B} r^2, \quad (64.46)$$

where r is the distance between the nuclei of A and B in the activated state. The atoms A and B have only translational degrees of freedom, and so the respective partition functions are

$$Q_A = \frac{(2\pi m_A kT)^{3/2}}{h^3} \quad \text{and} \quad Q_B = \frac{(2\pi m_B kT)^{3/2}}{h^3}. \quad (64.47)$$

It follows, therefore, from equation (64.44), by inserting the results of equations (64.45), (64.46) and (64.47), that

$$\begin{aligned} k_r &= \frac{kT}{h} \cdot \frac{\frac{\{2\pi(m_A + m_B)kT\}^{3/2}}{h^3} \cdot \frac{8\pi^2 I kT}{h^2} \cdot \frac{m_A m_B}{m_A + m_B} r^2}{\frac{(2\pi m_A kT)^{3/2}}{h^3} \cdot \frac{(2\pi m_B kT)^{3/2}}{h^3}} e^{-E_0/RT} \\ &= r^2 \left(8\pi kT \frac{m_A + m_B}{m_A m_B} \right)^{1/2} e^{-E_0/RT}. \end{aligned} \quad (64.48)$$

It is of interest to observe that this expression is identical with that based on the collision theory of reaction rates; however, it is only in this particular case, when the reaction involves two atoms, that the statistical theory described above leads to the same result as does the simple collision theory. For more complex reactions, both numerator and denominator in the rate equation (64.44) will contain the partition functions associated with a variety of internal degrees of freedom. As a result of the introduction of these additional factors, the specific rate is found to be much smaller than required by the collision theory, as is actually found in practice.

FREE AND RESTRICTED ROTATION .

65a. Internal Rotation.—If there is a possibility of free internal rotation within a molecule, it is necessary to make allowance for this in the total partition function; in the first place, the number of vibrational factors is

decreased by one for every type of internal rotation, but it must be replaced by a factor for each of the degrees of freedom of the latter type. The simplest molecule exhibiting internal rotation is ethane, in which there is rotation of two symmetrical tops, the methyl groups, about an axis coincident with the C—C bond; internal rotation of a similar character is possible in many organic compounds. Whenever a methyl, or other, group is attached to a molecular residue, internal rotation must be taken into consideration. In general, the simplest molecular structure in which internal rotation occurs, consists of a rigid framework to which one or more rigid symmetrical tops are attached. The term *symmetrical top* here refers to a rotating group (top), whose two moments of inertia about axes perpendicular to the top axis are equal. Such molecules have been called *pseudo-rigid*, because the external moments of inertia, i.e., of the molecule as a whole, are independent of the internal rotation. Examples of such pseudo-rigid molecules are all the methyl derivatives of methane, ethylene, benzene, water, hydrogen sulfide, ammonia and formaldehyde. It will be noted that while isobutane, methyl alcohol and methylamine fall into this category, *n*-butane, ethyl alcohol and ethylamine are not included.

Until relatively recent years, it was generally supposed that the rotation of a methyl group about the C—C bond in ethane, and similar compounds, was quite free and unrestricted. Although there are good reasons for changing this view, the consequences of completely free internal rotation will be considered first. The contribution to the partition function of a free internal rotator, forming part of a pseudo-rigid molecule, can be most easily derived by the classical method. If ϕ is the angle of rotation about the axis and p_ϕ is the conjugate momentum, the energy of rotation can be expressed in the Hamiltonian form [cf. equation (59.7)],

$$H(p, q) = \frac{1}{2I} p_\phi^2, \quad (65.1)$$

where I is the *reduced* moment of inertia of the rotating group, defined by

$$I = \frac{I_1 I_2}{I_1 + I_2},$$

I_1 and I_2 being the moments of inertia, about the axis of rotation, of the two parts of the molecule which are rotating with respect to each other. The classical partition function, exclusive of a symmetry factor, is then

$$\begin{aligned} Q_{ir} &= \frac{1}{h} \int_0^{2\pi} \int_{-\infty}^{\infty} e^{-p_\phi^2/2IkT} d\phi dp_\phi \\ &= \frac{2\pi}{h} (2\pi IkT)^{1/2} \\ &= \frac{(8\pi^3 IkT)^{1/2}}{h}. \end{aligned} \quad (65.2)$$

There still remains to be considered the question of the symmetry number; two procedures are possible. One is to include the total symmetry number for the external rotation, equation (62.5); the other is to split the total into two factors, one for external rotation, assuming a completely rigid molecule without internal rotation, and the other for the internally rotating groups. The latter procedure is the one generally adopted, so that the partition function for each internally rotating group is represented by

$$Q_{ir} = \frac{(8\pi^3 I k T)^{1/2}}{h \sigma_i} \quad (65.3)$$

where σ_i is the symmetry number of the internally rotating group.¹² The situation may be illustrated by reference to ethane; the total symmetry number of the molecule is 18, and this may be included in the rotational partition function as a whole. However, it is perhaps more convenient to consider the symmetry number of the molecule as made up of two factors. If the internal rotation were frozen, the symmetry number would be 6; this arises because of three equivalent positions resulting from rotation of the whole molecule through angles of $\frac{2}{3}\pi$, $\frac{4}{3}\pi$ and 2π , about the C—C axis, each of which is duplicated when the molecule is rotated through 180° about an axis perpendicular to that of the C—C bond. The symmetry number for internal rotation σ_i is 3, since the methyl group has three equivalent positions when rotated about the C—C axis. In writing the partition function of ethane, therefore, it is permissible to take σ as equal to 6 in equation (62.5), and to reserve the factor 3 for use with the contribution of the degree of freedom for internal rotation.

The classical treatment of the free internal rotator has been extended to the most general case of a molecule with $s - 3$ degrees of freedom of internal rotation, i.e., there are $s - 3$ internally rotating groups, and three degrees of freedom of external rotation, making s in all.¹³ The kinetic energy of rotation, including both external and internal forms, can be represented by the expression

$$T = \frac{1}{2} \sum_{i=1}^s \sum_{j=1}^s R_{ij} \dot{q}_i \dot{q}_j, \quad (65.4)$$

where the R_{ij} factors involve the q -coordinates which, in this case, are the three Eulerian angles, which orient the molecule as a whole (Section 62b), and $s - 3$ angles which orient the rotating groups. The kinetic energy may also be written in a form involving the momenta, viz.,

$$T = \frac{1}{2} \sum_{i=1}^s \sum_{j=1}^s P_{ij} p_i p_j, \quad (65.5)$$

¹² A factor that is equivalent to this symmetry number is frequently represented by n in the original literature.

¹³ Eidinoff and Aston, *J. Chem. Phys.*, 3, 379 (1935); Aston, ref. 1; Kassel, *J. Chem. Phys.*, 4, 276 (1936).

where the P_{ij} 's, which now contains the q 's, can be evaluated in terms of the R_{ij} 's of equation (65.4). Since all the rotations, internal and external, are assumed to be free, all the rotational energy will be kinetic, and hence equation (65.5) gives the total rotational energy in the Hamiltonian form. The classical expression for the complete rotational partition function is

$$Q_r = \frac{1}{\sigma h^s} \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} e^{-H(p, q)/kT} dq_1 \cdots dq_s dp_1 \cdots dp_s, \quad (65.6)$$

and if the value of $H(p, q)$ as given by equation (65.5) is inserted, and integration carried out with respect to the momenta, the result is

$$Q_r = \frac{1}{\sigma} \left(\frac{2\pi kT}{h^2} \right)^{s/2} \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} [R]^{1/2} dq_1 \cdots dq_s, \quad (65.7)$$

where $[R]$ is the determinant of the R_{ij} 's, i.e.,

$$[R] = \begin{vmatrix} R_{11}R_{12} & \cdot & \cdot & \cdot & R_{1s} \\ R_{21}R_{22} & \cdot & \cdot & \cdot & R_{2s} \\ \cdot & \cdot & & & \cdot \\ \cdot & \cdot & & & \cdot \\ \cdot & \cdot & & & \cdot \\ R_{s1}R_{s2} & \cdot & \cdot & \cdot & R_{ss} \end{vmatrix}. \quad (65.8)$$

In equation (65.7) the symmetry number σ refers to the value for the molecule as a whole, including both external and internal rotation.

In particular cases that are not too involved, equation (65.7) may be used to evaluate the rotational partition function, but some simplification is first possible. As mentioned above, the q 's include the three Eulerian angles, and integration can be carried out with respect to these variables. The result for the most general case is still complicated, but it can be considerably reduced for a pseudo-rigid molecule, in the sense defined above. For such a molecule, equation (65.7) becomes

$$Q_r = \frac{1}{\sigma} \left(\frac{2\pi kT}{h^2} \right)^{s/2} 8\pi^2 (2\pi)^{s-3} [S]^{1/2}, \quad (65.9)$$

in which $[S]$ is defined by

$$[S] = K_1 K_2 \cdots K_{s-3} \begin{vmatrix} I_{xx} - \lambda\lambda & -I_{xy} - \lambda\mu & -I_{xz} - \lambda\nu \\ -I_{xy} - \lambda\mu & I_{yy} - \mu\mu & -I_{yz} - \mu\nu \\ -I_{xz} - \lambda\nu & -I_{yz} - \mu\nu & I_{zz} - \nu\nu \end{vmatrix}.$$

In this expression K_1, K_2, \dots, K_{s-3} are the moments of inertia, about the bonds joining them to the rigid framework, of the $s-3$ internally rotating groups; $I_{xx}, I_{yy}, I_{zz}, I_{xy}, I_{xz}$ and I_{yz} have the same significance as in Section

62b, and

$$\lambda\mu = \sum_{i=1}^{s-3} \lambda_i \mu_i K_i,$$

with the other terms involving λ , μ and ν defined in a similar manner, where λ_i , μ_i and ν_i are the direction cosines of the axis of the i th group with respect to the axes x , y , z , fixed in the molecule.

The quantities with λ , μ and ν , in the determinant contained in $[S]$, which is part of the expression for the partition function as given by equation (65.9), arise because of the interaction between internal and external coordinates. If these terms are small, so that they can be neglected in comparison with the moments and products of inertia, I_{xx} , I_{yy} , I_{xy} , I_{xz} , etc., it is seen, by comparison with equation (62.6) that the determinant becomes equal to ABC , the product of the three principal (external) moments of inertia. In this event, equation (65.9) reduces to

$$Q_r = \frac{1}{\sigma} \left(\frac{2\pi kT}{h^2} \right)^{3/2} 8\pi^2 (2\pi)^{s-3} \{ K_1 K_2 \cdots K_{s-3} (ABC) \}^{1/2}. \quad (65.10)$$

The significance of this result can be seen if this expression is divided into two parts, as follows

$$Q_r = \left\{ \frac{8\pi^2 (8\pi^3 ABC) (kT)^{3/2}}{\sigma_e h^3} \right\} \left\{ \prod_{i=1}^{s-3} \frac{(8\pi^3 K_i kT)^{1/2}}{\sigma_i h} \right\}, \quad (65.11)$$

where the total symmetry number σ is equal to the product of the external factor σ_e , and the factors σ_i for the internally rotating groups. The expression in the first brackets in equation (65.11) is seen to be the same as equation (62.5), apart from the nuclear spin factor, and hence gives the contribution of the external rotation to the partition function; the quantity in the second brackets is the product of $s - 3$ terms of the form of equation (65.3). It appears, therefore, that it is possible, at least as a first approximation, not only to separate the contributions of the external and internal rotations to the partition function, but also to separate the factors for the individual rotating groups; thus, the result may be expressed briefly in the form

$$Q_r = Q_{er} \times \prod_{i=1}^{s-3} Q_{ir}, \quad (65.12)$$

where Q_{er} refers to external rotation, i.e., rotation of the molecule as a whole, and $\prod Q_{ir}$ is the product of the contributions of the $s - 3$ internally rotating groups considered separately. It will be noted that the internal rotation factors in equation (65.11) are not exactly identical with equation (65.3); the difference is that the former contains K_i , the moment of inertia of the rotating group, while in the latter the corresponding quantity is I , the reduced moment. It is probable that when the approximate equation (65.12) is used to calculate the complete rotational partition function, it is better to

use the reduced moment of inertia about the axis of rotation, rather than the actual value.

65b. Restricted Internal Rotation.—In the calculation of the thermodynamic properties of ethane by the method of partition functions, prior to the year 1936, it was generally assumed that the two methyl groups rotated freely with respect to each other about the C—C axis. It appeared, however, that this assumption led to results that were not in agreement with experiment, and the view developed that the rotation of the groups in ethane was not free, but was restricted in some manner.¹⁴ For example, the entropy of ethane determined experimentally, on the basis of the third law of thermodynamics, was found to be 49.54 cal./deg./mole at 184.1° K, and 54.85 cal./deg./mole at 298.1° K; the values calculated from partition functions at these temperatures, assuming completely free internal rotation, were 51.09 and 56.36 cal./deg./mole, respectively. Discrepancies were also found with other molecules in which free internal rotation had been expected; among these may be mentioned tetramethylmethane, *n*- and iso-butane, methyl and dimethylaniline, methyl, ethyl and isopropyl alcohols, silicon tetramethyl and acetone. In similar compounds that do not contain groups which might be capable of rotation, e.g., methyl chloride and bromide, methane, etc., no discrepancies were observed. It may be stated that in recent years evidence for the existence of restricted rather than free rotation of groups in organic compounds has accumulated, and the concept of restricted rotation is now widely accepted. It should be pointed out that this does not really contradict the views concerning "free rotation" about bonds, in so far as isomeric structures with different configurations do not exist. The reason why the two ideas do not conflict is that the energy barriers which prevent completely free rotation are of the order of 3 kcal., and so the rate at which one configuration changes into another is rapid at ordinary temperatures. The energy barriers restricting rotation would have to be much higher, e.g., about 20 kcal., if the different configurations were to be stable and different isomeric forms were to exist at ordinary temperatures.

65c. Potential Barrier Restricting Rotation.—For the development of the partition function of a molecule in which there are groups undergoing internal rotation that is restricted, rather than free, it is necessary to know, in the first place, how the restricting potential energy varies with the angle of rotation. No definite information is available as to the exact nature of the potential function that is appropriate to any particular case, but a simple expression, which is at least of the correct form, has been proposed. It is probable that the final results are not very sensitive to the exact shape of the barrier, as represented by this potential function. The general conditions which the function must satisfy can be seen by considering a simple case, such as the ethane molecule. For the sake of the argument, it will be supposed that the restriction to free rotation is due to the mutual repulsion of

¹⁴ Kemp and Pitzer, *J. Chem. Phys.*, 4, 749 (1936); *J. Am. Chem. Soc.*, 59, 276 (1937); see also, Smith and Vaughan, *J. Chem. Phys.*, 3, 341 (1935); Howard, *ibid.*, 5, 451 (1937).

the hydrogen atoms of one methyl group and those of the other methyl group. As the groups rotate about the C—C axis, the repulsion reaches a maximum when the configuration of the molecule is such that the hydrogen atoms in the two groups are opposite each other (eclipsed position). Upon continued rotation, the repulsion diminishes until the intermediate (staggered) position of the hydrogen atoms is reached; it then increases, until after a total rotation of $\frac{2}{3}\pi$ the eclipsed position, with a maximum repulsion, is again reached. It can be easily seen that the potential for the restriction of rotation in ethane should be of such a form as to lead to equal maxima at intervals of $\frac{2}{3}\pi$, with equal minima in between. In view of the symmetry of the rotating groups, it is evident that the potential function must satisfy these conditions, irrespective of the cause of the restriction in rotation.

In general, the potential function of a restricted internal rotator which, in the course of its rotation, passes through n equivalent positions may be represented by an equation of the form

$$V = \frac{1}{2}V_0(1 - \cos n\phi), \quad (65.13)$$

where V is the restricting potential when the angle of rotation is ϕ ; V_0 is the maximum height of the potential barrier. If the n positions are exactly equivalent, n is identical with the internal symmetry number σ_i , and so equation (65.13) becomes

$$V = \frac{1}{2}V_0(1 - \cos \sigma_i\phi). \quad (65.14)$$

For ethane, σ_i is 3, and so a possible expression for the restricting potential is

$$V = \frac{1}{2}V_0(1 - \cos 3\phi), \quad (65.15)$$

and this function is represented graphically in Fig. 44. It is seen that, as required, there are equal maxima,

spaced $\frac{2}{3}\pi$ apart, with minima between. Although it is not certain that the actual barrier is of the type represented by Fig. 44, it is reasonably sure that the general form is correct. Since the mathematical treatment of a potential function like equation (65.15) is relatively simple, this has invariably been used in the discussion of restricted internal rotation.

65d. Partition Function for Restricted Rotation.—In order to derive the partition function for restricted rotation, it is necessary to know something of the possible energy levels, and these can be derived, at least in principle, by means of wave mechanics.¹⁵ For the special case of a molecule, such as ethane, consisting of two identical symmetrical tops rotating about a

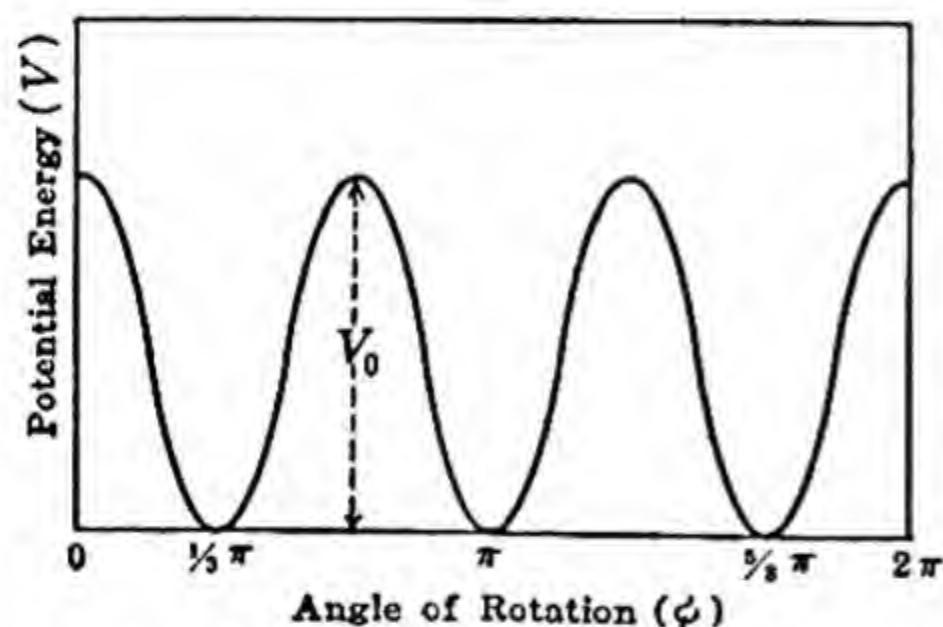


FIG. 44. Restricting potential for internal rotation in ethane

¹⁵ Pauling, *Phys. Rev.*, 36, 430 (1930); Nielsen, *ibid.*, 40, 445 (1932)

common axis, the treatment is not difficult, and so it will be given here. It is probable that the results hold, with a fair degree of approximation, to other pseudo-rigid molecules in which the rotating groups are not identical, provided the tops are of the symmetrical type.

The general wave equation for a restricted rotator is similar to that given by equation (9.21), with the addition of a potential energy term, viz.,

$$\frac{1}{\sin \theta} \cdot \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \cdot \frac{\partial^2 \psi}{\partial \phi^2} + \frac{8\pi^2 I}{h^2} (E - V) \psi = 0, \quad (65.16)$$

where I is here, as in Section 65a, the reduced moment of inertia of the rotating group. In the particular case under consideration the restricted rotation takes place about a definite axis, and so all terms involving θ may be ignored; the wave equation is now

$$\frac{\partial^2 \psi}{\partial \phi^2} + \frac{8\pi^2 I}{h^2} (E - V) \psi = 0, \quad (65.17)$$

where the eigenfunction is a function of the angle ϕ only. Inserting equation (65.15) for the potential energy V , the result is

$$\frac{\partial^2 \psi}{\partial \phi^2} + \frac{8\pi^2 I}{h^2} \{E - \frac{1}{2} V_0 (1 - \cos \sigma_1 \phi)\} \psi = 0. \quad (65.18)$$

If the variable is changed, by defining a new variable x as

$$x = \frac{1}{2} \sigma_1 \phi, \quad (65.19)$$

so that the function ψ is replaced by M , where

$$M(x) = \psi(\phi),$$

then

$$\frac{\partial^2 \psi(\phi)}{\partial \phi^2} = \frac{\sigma_1^2}{4} \cdot \frac{\partial^2 M(x)}{\partial x^2}.$$

It follows, therefore, that equation (65.18) can be written as

$$\frac{\partial^2 M}{\partial x^2} + \frac{32\pi^2 I}{\sigma_1^2 h^2} \{E - \frac{1}{2} V_0 (1 - \cos 2x)\} M = 0. \quad (65.20)$$

Two quantities a and q may now be defined in the following manner.

$$a = \frac{32\pi^2 I}{\sigma_1^2 h^2} (E - \frac{1}{2} V_0)$$

and

$$q = \frac{2\pi^2 I V_0}{\sigma_1^2 h^2},$$

and if these are introduced into equation (65.20), the result is

$$\frac{\partial^2 M}{\partial x^2} + (a + 16q \cos 2x)M = 0. \quad (65.21)$$

This differential equation is known to mathematicians as Mathieu's equation; it has solutions only for specific values of the Mathieu function $M(x)$. Many of these, together with the corresponding values of a as a function of q , have been tabulated. It follows, therefore, that if q is known, the possible eigensolutions a of equation (65.21) can be obtained, either from the tables or by calculation in a definite manner. From the definition given above, it is seen that q depends on the reduced moment of inertia I of the rotator, and on the maximum V_0 of the potential barrier; consequently, if these quantities are known, the permitted values of a , and hence of the energy E of the restricted rotator, can be determined. The partition function for restricted rotation can then be derived by direct summation of the $e^{-E/kT}$ terms, using the values of E calculated in the manner just described. The energy levels of the restricted rotator are nondegenerate, and so the statistical weight factor g is equal to unity in each case.

65e. Evaluation of Restricting Potentials.¹³—If the approximation is made of regarding external and internal rotations as independent, the foregoing treatment provides, in principle, a solution to the problem of the restricted rotator, in the simpler cases. The difficulty in applying the results arises because there is, as yet, no independent method of evaluating the height V_0 of the energy barrier restricting the rotation. Approximate indications of the magnitude may possibly be derived from spectroscopic data or from quantum mechanics, but these are not sufficiently accurate for the calculation of partition functions. The procedure that has been adopted hitherto, therefore, is to estimate the value of the restricting potential V_0 that is necessary to make the calculated thermodynamic property, such as entropy, heat capacity or free energy, equal to the value determined by direct experiment. The magnitude of the particular property due to electronic multiplicity (if any), translation, vibration and external rotation is subtracted from the observed value; the difference is then due to restricted (or free) internal rotation, and the potential V_0 necessary to account for this difference can be evaluated. An alternative treatment, which is fundamentally the same as that just described, is to calculate the value of the thermodynamic property on the assumption that the internal rotation is completely free, and then to find the restricting potential that will correspond to the discrepancy between this figure and the experimental result.

In order to facilitate these computations, double-entry tables have been prepared in which the value of the entropy, heat capacity or free energy for restricted rotation is given as a function of V_0/RT and of another variable. In the earlier tabulations this second function was σ_i^2/IV_0 , which is seen to

¹³ Pitzer, *J. Chem. Phys.*, 5, 469, 473 (1937); Pitzer and Gwinn, *ibid.*, 10, 428 (1942); see also, Pitzer, *ibid.*, 8, 711 (1940); *Chem. Rev.*, 27, 39 (1940).

be proportional to $1/q$, but since both variables contained the unknown V_0 , there was a slight difficulty in their use; it was necessary to utilize also their product from which V_0 was eliminated. In the more recent tables, the second function is $1/Q_{fr}$ where Q_{fr} is the partition function for internal rotation if this is completely free, e.g., equation (65.2), (65.11) and (65.12). These tables are, of course, much simpler to use, since Q_{fr} can be readily calculated and requires no knowledge of the restricting potential. The principle employed in the preparation and use of these tables is briefly as follows. A series of arbitrary values of V_0/RT , from zero to 20.0, and of $1/Q_{fr}$, from zero to about 0.8, are taken; noting the definition of Q_{fr} , as given, for example, by equation (65.2), it is seen that the product of V_0/RT and Q_{fr}^2 is proportional to $IV_0/\sigma_i^2 h^2$, and hence is related to the variable q of the Mathieu equation. Each pair of arbitrary values of V_0/RT and $1/Q_{fr}$ thus yields a value of q , and this is found, from the tables of Mathieu functions, or from the analogous calculations, to correspond to a series of permitted a values. It is from these that the eigenvalues of the energy of the restricted rotator can be derived. The equation giving the definition of a may be put into the form

$$a = 32\pi^2 \frac{IkT}{\sigma_i^2 h^2} \left(\frac{E}{kT} - \frac{V_0}{2kT} \right).$$

The appropriate values of $IkT/\sigma_i^2 h^2$ and of $V_0/2kT$ are obviously determinable directly from the arbitrarily chosen V_0/RT and $1/Q_{fr}$, since Q_{fr}^2 is equal to $8\pi^3 IkT/\sigma_i^2 h^2$; consequently, the permitted values of E/kT , which are the quantities required for the evaluation of the partition function for the restricted rotator, can be obtained from the known a values. The procedure is repeated for every combination of the arbitrary values of V_0/kT and $1/Q_{fr}$, and the partition function is determined by actual summation of the $e^{-E/kT}$ terms in each case. From a knowledge of the allowable E/kT values it is possible to calculate also the temperature derivatives of the partition function (cf. Section 56c); hence the contributions to various thermodynamic properties of the restricted rotator, for a given V_0/RT and $1/Q_{fr}$ can be evaluated. In this way, the information for the preparation of the double-entry tables is made available. The calculations are, of necessity, carried out for a number of specific (rounded) values of the two variables, but the results for intermediate case can be readily derived by graphical interpolation.

In using the tables to determine V_0 , the maximum of the restricting potential barrier, the value of a particular thermodynamic property must first be obtained by direct experiment. The contributions of all degrees of freedom, except that for internal rotation, are then calculated from the partition functions in the usual manner. Subtraction of this value from the experimental result gives the contribution to the thermodynamic property of the restricted rotation. From this datum and $1/Q_{fr}$, obtained by means of equation (65.2), the double entry tables can be used to give the appropriate V_0/kT . Since the temperature is known, the restricting potential V_0 is determined.

Although the foregoing treatment should strictly be applied to cases involving a restricted rotator consisting of two coaxial tops, it appears from an extension of the calculation that the results apply with sufficient accuracy to any case of a pseudo-rigid molecule, provided the n maxima in the potential function are almost identical. It should be noted, however, that although the tables referred to above may be used for evaluating the potential function maximum V_0 in all cases of pseudo-rigid molecules, the number of maxima n will not necessarily be the same as the symmetry number σ_i . The former must be used in the calculations of the energy levels of the restricted rotator, but the latter should be included in the partition function.

65f. Alternative Calculation of Restricting Potential.¹⁷—An alternative method for evaluating the contribution to various thermodynamic properties of a symmetrical top undergoing hindered rotation makes use of the fact that in the lower energy levels the movement is approximately vibrational in character, whereas the higher levels approach pure (free) rotational behavior. When the energy of the rotator is well below the maximum of the potential barrier, the rotating group undergoes a torsional oscillation (libration) that is virtually a vibration. On the other hand, for energy levels that are in the neighborhood of, or above, the maximum V_0 of the barrier, the group will rotate freely. These conclusions may be reached in a more precise manner, as will be shown in the following paragraphs.

According to the trigonometrical relationship

$$1 - \cos \sigma_i \phi = 2 \sin^2 \frac{1}{2} \sigma_i \phi,$$

the expression for the potential function, equation (65.15), becomes

$$V = V_0 \sin^2 \frac{1}{2} \sigma_i \phi. \quad (65.22)$$

For the lower energy levels of the hindered rotator, the angle of rotation ϕ is always small, and hence it is possible to make use of the approximation $\sin x \approx x$, which is applicable under these conditions; hence

$$\sin \frac{1}{2} \sigma_i \phi \approx \frac{1}{2} \sigma_i \phi,$$

so that

$$V = V_0 \left(\frac{1}{2} \sigma_i \phi \right)^2. \quad (65.23)$$

The general expression for the potential energy of a harmonic oscillator is $V = \frac{1}{2} f q^2$, and for a torsional harmonic oscillation, or libration, this takes the form

$$V = \frac{1}{2} f \phi^2, \quad (65.24)$$

and the corresponding oscillation frequency is

$$\nu = \frac{1}{2\pi} \sqrt{\frac{f}{I}}, \quad (65.25)$$

¹⁷ Crawford, *J. Chem. Phys.*, 8, 273 (1940); Price, *ibid.*, 9, 807 (1941); Wilson, *Chem. Rev.*, 27, 17 (1940); see, however, Pitzer and Gwinn, *J. Chem. Phys.*, 9, 485 (1941).

where I , as before, is the reduced moment of inertia. Comparison of equations (65.23) and (65.24) shows that the lower energy levels of the restricted rotator are equivalent to a libration, as mentioned previously. The appropriate force constant f is given by

$$f = \frac{1}{2} V_0 \sigma_i^2,$$

and hence by equation (65.25) the corresponding frequency of oscillation is

$$\nu = \frac{\sigma_i}{2\pi} \sqrt{\frac{V_0}{2I}}. \quad (65.26)$$

For the higher energy levels of the restricted rotator, on the other hand, it is possible to neglect the potential energy V in comparison with the total energy E ; the wave equation (65.17) then becomes

$$\frac{\partial^2 \psi}{\partial \phi^2} + \frac{8\pi^2 I E}{h^2} \psi = 0,$$

which is the equation for a completely unhindered rigid rotator with fixed axis. In the higher levels the restricted rotator may thus be treated as rotating freely.

The suggestion has been made that the partition function for a hindered rotator may be separated into two appropriately weighted parts; one represents the summation over the lower energy levels which are vibrational in character, while the other is the summation over the upper levels having the properties of a free rotator. The energy values are determined, as before, from the solutions of the Mathieu equation (65.21), but the significance of the variables a and q is modified somewhat so as to allow for interaction effects in the molecule. The partition function is then given by

$$Q_{rr} = (\Omega^{1/2} G_r + G_v),$$

where G_r represents the sum over the upper "rotational" levels, and G_v is the sum over the lower "vibrational" levels; the factor Ω is defined by

$$\Omega = 1 - D \left(\frac{\lambda_A^2}{A} + \frac{\lambda_B^2}{B} + \frac{\lambda_C^2}{C} \right),$$

in which A , B and C are the principal moments of inertia of the whole molecule, D is the moment of the rotating group about its axis of rotation, and λ_A , λ_B and λ_C are the cosines of the angles between the group axis and the principal axis of the molecule. The quantity Ω evidently allows for the interaction of the rotation of the group under consideration with the rotation of the molecule as a whole; when Ω is unity, and the interaction is negligible, the results obtained by the method under discussion become identical with those previously described.

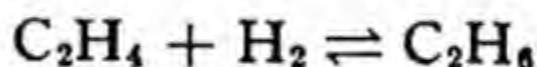
The evaluation of thermodynamic properties of the hindered rotator by this alternative procedure, if the maximum potential V_0 is known, or vice versa, is also facilitated by means of tables. The calculations appear to be slightly more involved than in the other method. However, the question of which treatment is the more accurate is still a matter for controversy.

65g. Application of Restricted Rotation Potentials.—The potentials restricting rotation in a number of simple molecules have been determined, by the procedures described in the foregoing sections, with the aid of both heat capacity and entropy measurements.¹⁸ Some of the results obtained are recorded in Table XXI; the actual values are dependent on the form of the postulated potential function [equation (65.13)], but the deviations are probably small.

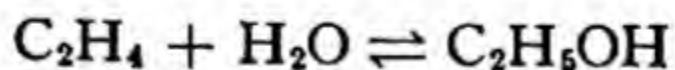
TABLE XXI. POTENTIALS RESTRICTING FREE INTERNAL ROTATION

Substance	V_0	Substance	V_0
Ethane	2.75 kcal.	Methylamine	3.00 kcal.
Propane	3.40	Methyl alcohol	3.40
Propylene	2.12	Acetone	1.00
Tetramethylmethane	4.50	Dimethylacetylene	<0.50

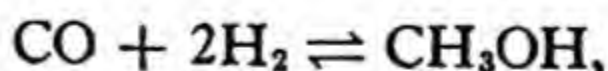
The importance of a knowledge of the restricting potential lies in the fact that once it has been determined, e.g., from a single heat capacity measurement, for a given substance, it can be applied to the calculation of any of the thermodynamic properties of that substance at any temperature. For example, in the derivation of the free energy change, or equilibrium constant, of the reaction



from partition functions, use is made of the restricting potential V_0 of 2.75 kcal. in ethane, obtained from a comparison of the observed heat capacity of this substance with the calculated value. With this restricting potential the correct value of the free energy function for ethane can be derived, and hence the free energy change of the aforementioned reaction can be determined. The equilibrium constants calculated in this manner are in excellent agreement with the best experimental values over the temperature range from 673° to 973° K.¹⁹ Similar calculations have been made for other equilibria, e.g.,



and



involving substances in which there is restriction to internal rotation.

¹⁸ Kistiakowsky, *et al.*, *J. Chem. Phys.*, 6, 18, 407, 900 (1938); 7, 289 (1939); 8, 610, 970 (1940); Aston, *et al.*, *J. Am. Chem. Soc.*, 59, 1743 (1937); 61, 1539 (1939); *J. Chem. Phys.*, 6, 480, 485 (1938); 8, 743 (1940); *Chem. Rev.*, 27, 59 (1940); Kemp and Egan, *J. Am. Chem. Soc.*, 60, 1521 (1938); Crawford, *J. Chem. Phys.*, 8, 744 (1940); Telfair, *ibid.*, 10, 167 (1942); Thompson, *Ann. Rep. Chem. Soc.*, 38, 49 (1941).

¹⁹ Guggenheim, *Trans. Faraday Soc.*, 37, 97, 271 (1941); Kistiakowsky, *J. Chem. Phys.*, 10, 78 (1942).

CHAPTER IX

INTERMOLECULAR FORCES¹

MOLECULAR POTENTIAL FUNCTION

66a. Attraction Between Molecules.—The very existence of liquids and the occurrence of such phenomena as the Joule-Thomson effect indicate that there must be attractive forces between molecules even when they cannot interact chemically. These forces of attraction are generally referred to as *van der Waals forces*, because van der Waals made allowance for their effect in the familiar equation of state that bears his name. Although the existence of molecular attractive forces has been accepted for many years, it is only in recent times that a satisfactory explanation of their origin has been proposed. It is easy to understand that a molecule possessing a resultant dipole will attract another dipolar molecule, whether it be of the same kind or not, by ordinary electrostatic forces. Similarly, a molecule with a permanent dipole will attract a nonpolar (homopolar) molecule as a result of the induction of a dipole by the former in the latter. However, there is no doubt that van der Waals attractive forces exist between two nonpolar or symmetrical molecules, such as hydrogen, oxygen, nitrogen, carbon dioxide, methane, and the inert gases, among others; in these cases electrostatic, or coulombic, forces of the usual kind cannot account for the attraction. An important suggestion concerning the origin of the attractive forces, which involve nonpolar as well as dipolar molecules, was made by London.²

The fundamental basis of the theory is that as a direct consequence of the uncertainty principle, the nuclei and electrons of every molecule, even a monatomic molecule, must be regarded as undergoing some kind of oscillation with respect to each other. An instantaneous picture of all the molecules in a gas, for example, should show various relative displacements of nuclei and electrons, that is, of positive and negative charges; such displacements are equivalent to the possession of dipole moments by the molecule. The magnitude of the dipole moment of each molecule is not constant, but will vary with the relative displacements of nuclei and electrons at any instant. As a result of the oscillations of these particles, every molecule of a gas, whether it has permanent polarity or not, behaves as an oscillating dipole. If the molecule possesses no permanent moment, that is to say, if it is of the type generally described as nonpolar or homopolar, these rapidly

¹ Fowler, "Statistical Mechanics"; Fowler and Guggenheim, "Statistical Thermodynamics"; Margenau, *Rev. Mod. Phys.*, 11, 1, 25 (1939); Mayer and Mayer, "Statistical Mechanics"; Mott and Gurney, *Rep. Progress Phys.* (Phys. Soc. London), 5, 146 (1938); General Discussion, *Trans. Faraday Soc.*, 33, 1-282 (1937).

² London, *Z. phys. Chem.*, B11, 222 (1930); *Z. Physik*, 60, 491 (1930); *Trans. Faraday Soc.*, 33, 8 (1937).

varying dipoles give a resultant of zero when averaged over a large number of configurations, that is, over a period of time. Nevertheless, the temporary dipoles are able to induce, in other molecules, dipoles that are in phase with themselves so that there is a resultant attraction between the molecules.

66b. Linear Oscillating Dipoles.—An indication of the manner in which the magnitude of the interaction may be calculated can be seen by considering the relatively simple case of two interacting molecules treated as equivalent to linear harmonic oscillators, free to oscillate along the same straight line.³

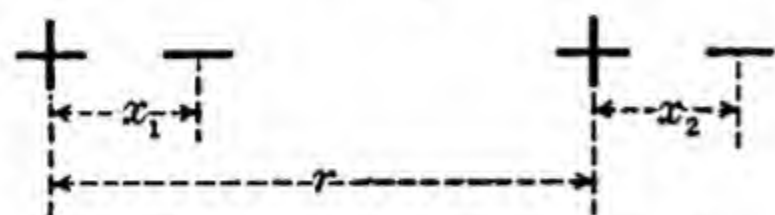


FIG. 45. Linear oscillating dipoles

Suppose that at any instant the displacement of the nuclei and electrons is x_1 in one molecule and x_2 in the other, as shown in Fig. 45; let r be the distance between the

positive ends of the two resultant dipoles. The mutual potential energy of these dipoles may now be calculated by means of Coulomb's law; according to this law, the potential energy of a system of two charges of magnitude e separated by a distance d in a medium of dielectric constant unity, which is assumed to be the case here, is equal to e^2/d . Hence it is readily seen from Fig. 45, that for the four possible interactions between the two charges on one dipole with the two charges on the other, the mutual potential energy V_e due to electrostatic forces is given by

$$V_e = e^2 \left(\frac{1}{r} + \frac{1}{r + x_2 + x_1} - \frac{1}{r - x_1} - \frac{1}{r + x_2} \right), \quad (66.1)$$

in which the positive terms give the interaction between charges of the same sign, while the negative terms refer to charges of opposite sign. If the difference between x_1 and x_2 is not large, at least in comparison with r , it follows that

$$\begin{aligned} V_e &= e^2 \left(\frac{2}{r} - \frac{1}{r - x_1} - \frac{1}{r + x_2} \right) \\ &\approx e^2 \left\{ \frac{2}{r} - \frac{2r}{(r - x_1)(r + x_2)} \right\} \\ &\approx -e^2 \frac{2x_1x_2}{r(r - x_1)(r + x_2)}. \end{aligned} \quad (66.2)$$

If r is large compared with x_1 and x_2 , as is very probable, this expression may be reduced to the simple form

$$V_e = -\frac{2e^2x_1x_2}{r^3}. \quad (66.3)$$

In addition to the electrostatic contribution to the potential energy of the dipole, allowance must be made for the ordinary (displacement) potential

³ Lennard-Jones, *Proc. Phys. Soc.*, (London), 43, 461 (1931).

energy of the oscillators. This is equal to $\frac{1}{2}fx_1^2 + \frac{1}{2}fx_2^2$, where f is the appropriate force constant; it follows, therefore, that the total potential energy of the system is given by

$$V = \frac{1}{2}f(x_1^2 + x_2^2) - \frac{2\epsilon^2 x_1 x_2}{r^3}. \quad (66.4)$$

It will be observed that when the two oscillators are relatively far apart, i.e., when r is large, the last term in equation (66.4) is negligible, and the potential energy corresponds to that of two oscillators having the same restoring force constant f , and the same frequency ν_0 determined by

$$\nu_0 = \frac{1}{2\pi} \sqrt{\frac{f}{\mu}}, \quad (66.5)$$

where μ is the reduced mass of each oscillator.

The complete wave function of the system of two oscillators may be written as

$$\frac{\partial^2 \psi}{\partial x_1^2} + \frac{\partial^2 \psi}{\partial x_2^2} + \frac{8\pi^2 \mu}{h^2} \left(E - \frac{1}{2}fx_1^2 - \frac{1}{2}fx_2^2 + \frac{2\epsilon^2 x_1 x_2}{r^3} \right) \psi = 0, \quad (66.6)$$

and in order to solve this equation in a simple manner it is convenient to make a normal coordinate transformation (cf. Section 34a) by introducing the new coordinates z_1 and z_2 , defined by

$$z_1 = \frac{1}{\sqrt{2}} (x_1 + x_2) \quad \text{and} \quad z_2 = \frac{1}{\sqrt{2}} (x_1 - x_2).$$

It follows, therefore, that

$$x_1 = \frac{1}{\sqrt{2}} (z_1 + z_2)$$

$$x_2 = \frac{1}{\sqrt{2}} (z_1 - z_2)$$

and

$$x_1 x_2 = \frac{1}{2} (z_1^2 - z_2^2).$$

Introduction of these quantities into equation (66.6) yields

$$\frac{\partial^2 \psi}{\partial z_1^2} + \frac{\partial^2 \psi}{\partial z_2^2} + \frac{8\pi^2 \mu}{h^2} (E - \frac{1}{2}f_1 z_1^2 - \frac{1}{2}f_2 z_2^2) \psi = 0, \quad (66.7)$$

where

$$f_1 = f - \frac{2\epsilon^2}{r^3} \quad \text{and} \quad f_2 = f + \frac{2\epsilon^2}{r^3}. \quad (66.8)$$

It is apparent that equation (66.7) can be separated into two independent

differential equations, so that

$$\frac{\partial^2 \psi}{\partial z_1^2} + \frac{8\pi^2\mu}{h^2} (E_1 - \frac{1}{2}f_1 z_1^2) \psi_1 = 0 \quad (66.9)$$

and

$$\frac{\partial^2 \psi}{\partial z_2^2} + \frac{8\pi^2\mu}{h^2} (E_2 - \frac{1}{2}f_2 z_2^2) \psi_2 = 0, \quad (66.10)$$

where the product of $\psi_1(z_1)$ and $\psi_2(z_2)$, is equal to ψ , and E_1 and E_2 add up to the total energy E . It is evident from a consideration of the case of the harmonic oscillator treated in Section 8 that the solutions of equations (66.9) and (66.10) are

$$E_1 = (n_1 + \frac{1}{2})h\nu_1$$

and

$$E_2 = (n_2 + \frac{1}{2})h\nu_2,$$

so that the eigensolutions of equation (66.7), giving the possible energy values E of the system of two linear dipolar oscillators, is represented by

$$E = (n_1 + \frac{1}{2})h\nu_1 + (n_2 + \frac{1}{2})h\nu_2, \quad (66.11)$$

where ν_1 and ν_2 are the frequencies of the interacting oscillators.

The values of ν_1 and ν_2 can be expressed in terms of the respective force constants f_1 and f_2 , given by equation (66.8), by means of the familiar relationship of the type of equation (66.5); thus

$$\begin{aligned} \nu_1 &= \frac{1}{2\pi} \left\{ \frac{1}{\mu} \left(f - \frac{2\epsilon^2}{r^3} \right) \right\}^{1/2} \\ &= \frac{1}{2\pi} \left\{ \frac{f}{\mu} \left(1 - \frac{2\epsilon^2}{fr^3} \right) \right\}^{1/2} \\ &= \nu_0 \left(1 - \frac{2\epsilon^2}{fr^3} \right)^{1/2}, \end{aligned} \quad (66.12)$$

after introducing the definition of ν_0 given by equation (66.5). In an exactly similar manner, it follows that

$$\nu_2 = \nu_0 \left(1 + \frac{2\epsilon^2}{fr^3} \right)^{1/2}. \quad (66.13)$$

It was seen above that when far apart, i.e., in the unperturbed state, the two oscillators may be regarded as having the same frequency ν_0 , but it is evident from equations (66.12) and (66.13) that when the oscillators are sufficiently close to interact, they behave as if they are vibrating with different frequencies, one (ν_1) being less than ν_0 and the other (ν_2) being greater than ν_0 . This is, of course, an illustration of the phenomenon of resonance. The energy of the system in the lowest energy state, i.e., the zero-point energy, is obtained by putting both n_1 and n_2 in equation (66.11)

equal to zero; the result is

$$E_0 = \frac{1}{2}h(\nu_1 + \nu_2),$$

and if the values of ν_1 and ν_2 given by equations (66.12) and (66.13) are introduced, it follows that

$$E_0 = \frac{1}{2}h\nu_0 \left\{ \left(1 - \frac{2\epsilon^2}{fr^3} \right)^{1/2} + \left(1 + \frac{2\epsilon^2}{fr^3} \right)^{1/2} \right\}.$$

Expanding the square roots in the brackets by means of the binomial theorem, and neglecting terms beyond the second, which is permissible since $2\epsilon^2/fr^3$ is not large, it is readily found that

$$E_0 = h\nu_0 \left(1 - \frac{\epsilon^4}{2f^2r^6} \right). \quad (66.14)$$

The zero-point energy of each oscillator is $\frac{1}{2}h\nu_0$, and so the sum for the two oscillators is $h\nu_0$; if this result is subtracted from the energy E_0 , the interaction, or coupling, energy $u(r)$, expressed as a function of the intermolecular distance r , is seen to be

$$u(r) = -\frac{h\nu_0\epsilon^4}{2f^2r^6}. \quad (66.15)$$

The negative value of the interaction energy signifies an attraction between the molecules, and this would represent the van der Waals energy for a pair of linear oscillators.

66c. Dispersion Forces.⁴—In actual fact, of course, molecules are capable of oscillating in three directions, and the method of calculation described above must be appropriately extended. Without going into the somewhat complex details, it may be stated that the result is analogous to equation (66.15); it is found, in fact, that the total interaction energy for a pair of three-dimensional isotropic oscillators is

$$u(r) = -\frac{3h\nu_0\epsilon^4}{4f^2r^6}. \quad (66.16)$$

This expression may be put into a more practical form by introducing other properties of the molecules.

If a molecule, placed in an electric field of strength F , acquires an induced dipole of moment μ_i , then this moment is related to the field strength by the expression $\mu_i = \alpha F$, where α is the polarizability of the molecule (cf. Section 33b). If x is the relative displacement of the unit charges ϵ in the dipole then, by definition, the dipole moment μ_i is given by

$$\begin{aligned} \mu_i &= \alpha F = x\epsilon, \\ \therefore F &= \frac{\epsilon}{\alpha} x. \end{aligned} \quad (66.17)$$

⁴ London, ref. 2.

The potential energy V_i of the induced dipole is obtained by multiplying the field strength F and the magnitude ϵ of the displaced charge, by the displacement dx , and integrating over the range from zero to x ; thus

$$\begin{aligned} V_i &= \int_0^x F \epsilon dx \\ &= \epsilon \int_0^x F dx. \end{aligned}$$

Introducing the value of F given by equation (66.17), it follows that

$$\begin{aligned} V_i &= \frac{\epsilon^2}{\alpha} \int_0^x x dx \\ &= \frac{\epsilon^2 x^2}{2\alpha} \\ &= \frac{1}{2} \alpha F^2. \end{aligned} \tag{66.18}$$

The displacement potential energy ($\frac{1}{2}fx^2$) of the oscillator in the earlier discussion may be regarded as arising from the displacement of the positive and negative charges, i.e., nuclei and electrons, in an electric field; it is thus possible to equate this quantity to the potential energy given by equation (66.18), viz.,

$$\begin{aligned} \frac{1}{2}fx^2 &= \frac{1}{2}\alpha F^2, \\ \therefore \alpha &= \frac{fx^2}{F^2}. \end{aligned} \tag{66.19}$$

Since F is equal to $\epsilon x/\alpha$, as given by equation (66.17), it follows immediately that

$$\alpha = \frac{\epsilon^2}{f}, \tag{66.20}$$

and if this result is introduced into equation (66.16), it is seen that the interaction energy $u(r)$ for the three-dimensional oscillator is given by

$$u(r) = - \frac{3h\nu_0\alpha^2}{4r^6}. \tag{66.21}$$

This energy is frequently referred to as the *dispersion energy*, and the corresponding part of the van der Waals forces is called the *dispersion forces*. The reason for the use of this adjective is because the oscillators producing the attractive forces are also responsible for the dispersion of light by the particular molecules.

The polarizability α may be calculated from the refractive index n for light of long wave length by means of the expression

$$\frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{\rho} = \frac{4}{3}\pi N\alpha, \tag{66.22}$$

where M is the molecular weight of the gas, and ρ is its density; N is the Avogadro number. Alternatively, for a molecule that does not possess a permanent dipole moment, use may be made of the expression

$$\alpha = \frac{1}{8}d^3,$$

where d is the diameter of the molecule, regarded as a perfectly conducting sphere.

The hypothetical unperturbed frequency ν_0 can be derived from measurements on the dispersion of light by the gas under consideration; the necessary information is, however, rarely available, and so an approximate procedure is adopted. According to classical electromagnetic theory, an oscillator of a certain frequency will emit radiation of that frequency; the maximum frequency ν_m of the radiation that can be emitted by a given atom or molecule is determined by its ionization potential I and the electronic charge e , such that

$$Ie = h\nu_m.$$

As an approximation, when other data are not available, ν_m may be identified with ν_0 in equation (66.21), and then the latter becomes

$$u(r) = -\frac{3Ie\alpha^2}{4r^6},$$

where I is, as usual, expressed in volts and e in coulombs, thus giving the dispersion energy in joules. Some justification for this approximation is found in the fact that in the cases for which ν_0 has been derived from optical dispersion measurements, the results generally agree, within a few per cent, with those obtained from the ionization potential.

It will be noted that the dispersion forces have been referred to as part of the van der Waals attractive forces. Actually for a molecule not possessing a permanent dipole moment, this is believed to constitute the whole of the van der Waals attraction. For dipolar molecules, however, there are additional forces due to the mutual attraction of the dipoles (orientation effect), and to the attraction between a dipolar molecule and the dipole it induces in an adjacent molecule (induction effect). The expressions for these two interaction forces are as follows:

$$\text{Orientation effect} = -\frac{2\mu^4}{3r^6kT} \quad (66.24)$$

$$\text{Induction effect} = -\frac{2\alpha\mu^2}{r^6}, \quad (66.25)$$

where μ is the permanent dipole moment. The relative magnitudes of the orientation, induction and dispersion effects for a number of homopolar and dipolar molecules are given in Table XXII. It is seen that the disper-

sion effect alone is capable of producing considerable molecular attraction, and only for substances with relatively high dipole moments is the orientation effect of any great importance; the induction effect is always very small. For most simple molecules, therefore, the van der Waals attraction is almost exclusively determined by the dispersion forces.

TABLE XXII. RELATIVE MAGNITUDES OF MOLECULAR INTERACTION FORCES³

Molecule	Dipole Moment	Orientation Effect	Induction Effect	Dispersion Effect
H ₂	—	—	—	11.3
A	—	—	—	57
N ₂	—	—	—	62
CH ₄	—	—	—	117
Cl ₂	—	—	—	461
HCl	1.03×10^{-18}	18.6	5.4	105
NH ₃	1.5	84	10	93
H ₂ O	1.8	190	10	47

The results given above for the dispersion effect allow for the interaction between a dipole in one molecule with a dipole in another; the calculation has been extended to include dipole-quadrupole and quadrupole-quadrupole interactions. The former of these is represented by a term involving r^{-8} and the latter by r^{-10} ; for most purposes, however, these may be neglected.

66d. Repulsive Forces: Complete Potential Function.—So far account has been taken only of the attractive forces between molecules; however, it is obvious that repulsive forces must exist, otherwise two molecules would not repel one another after impact. The quantum mechanical treatment⁵ of a system of two atoms or two molecules must evidently give the correct form, at least, of the repulsive forces, as is apparent from the shape of the potential energy curve obtained in this manner for a number of cases, e.g., Fig. 9 for two hydrogen atoms; it is seen that at relatively large distances the attractive forces predominate, but at short distances the repulsive forces are of chief importance, as is to be anticipated. According to the calculations of wave mechanics, the repulsive potential should be represented by an expression of the form $R(r)e^{-r/\rho}$, where $R(r)$ is a polynomial containing positive and negative powers of r , the intermolecular distance, and ρ is a constant for the given molecules. As a first approximation the polynomial may be replaced by a constant, yielding $Pe^{-r/\rho}$, but even this simpler expression for the repulsive potential is not very amenable to mathematical treatment. It has become the practice, therefore, to utilize an even simpler form, i.e., Ar^{-n} , where A and n are constants; in spite of its somewhat approximate nature, this gives results which are fairly satisfactory in most cases. The attractive potential, as developed in the preceding sections, may be represented by $-Br^{-m}$, where B is a constant for the given substance,

⁵ Slater and Kirkwood, *Phys. Rev.*, **37**, 682 (1931); Born and Mayer, *Z. Physik*, **75**, 1 (1932); Huggins, *J. Chem. Phys.*, **5**, 143 (1937); Buckingham, *Proc. Roy. Soc., A*, **168**, 264 (1938).

and m is probably equal to 6 in most cases; hence the complete potential function for the interaction of two molecules may be written in the form

$$u(r) = Ar^{-n} - Br^{-m}. \quad (66.26)$$

Application of this equation, often referred to as the *bireciprocal potential function*, will be made later; it will be seen that n may be taken as approximately equal to 12 for several gases.

SYSTEMS OF DEPENDENT PARTICLES

67a. The Phase Integral.—In the treatment of gases in Chapter VII, it was frequently mentioned that the particles (or molecules) were assumed to interact weakly with one another. The results can thus be regarded as applicable only to perfect gases or to those which do not depart markedly from ideal behavior; for conditions in which the mutual attraction of the molecules is appreciable, the conclusions of the previous chapter require some modification. In an ideal gas the energy of a molecule is independent of its positional coordinates, and has a definite value; it is thus possible to derive equations, such as the Maxwell-Boltzmann equation, for the distribution of molecules with respect to their *individual* energies. If the gas is imperfect, however, this is no longer possible, as will be evident from the following arguments. Consider, for simplicity, a system consisting of two molecules only; when these molecules are far apart, each will have a definite energy. As the molecules are brought together, however, they begin to interact, in the sense that forces of attraction and repulsion are operative. The energy of each molecule will then depend on its position with respect to the other molecule. The individual molecular energies are thus no longer definite quantities, and a distribution law involving these energies has no significance. In general, the energy of the pair of molecules may be expected to depend on their velocities, as well as on their positional coordinates. However, if the speeds are small in comparison with the rates of electronic and nuclear motions, the energy of the molecules may be regarded as dependent only on their position. For this reason, it is the practice to treat the interaction energy between molecules as being exclusively potential energy whose magnitude depends on the coordinates only.

In order to use the methods of statistical mechanics in connection with a system of particles that interact appreciably, that is, a system of *dependent particles*, as it is sometimes called, it is necessary to define a partition function for the whole system of molecules, rather than for an individual molecule, as was done in the treatment of perfect gases. This partition function, apart from the factor $1/h^f$, where f is the total number of degrees of freedom of the system, is equivalent to the Gibbs *phase integral*. For simplicity the classical formula for the partition function will be employed; under the majority of ordinary conditions this is quite satisfactory. Further, the assumption will be made that the potential energy of molecular interaction

does not affect the energies associated with internal degrees of freedom; in other words, the potential energy is dependent on the external (positional) and not on the internal coordinates. The contribution of the internal degrees of freedom to the partition function of each molecule will thus be the same as for a system of weakly interacting particles. The potential energy due to interaction, since it depends on the coordinates of position, will then be considered in conjunction with the translational energy in the evaluation of the partition function.

67b. Partition Function for System of Independent Particles.—It is convenient in the derivation of the partition function of a system of dependent particles to consider first a system of weakly interacting, or independent, particles; the results may then be compared directly with those obtained in Chapter VIII. If a system consists of N identical molecules which do not interact, the classical expression for the partition function due to $3N$ external degrees of freedom will be given by

$$Q_e = \frac{1}{N!} \cdot \frac{1}{h^{3N}} \int \cdots \int e^{-H(p,q)/kT} dq_1 \cdots dq_{3N} dp_1 \cdots dp_{3N}, \quad (67.1)$$

where $dq_1 \cdots dq_{3N}$ is equivalent to $dx_1 dy_1 dz_1 dx_2 dy_2 dz_2 \cdots dx_N dy_N dz_N$, the positional coordinates of the i th particle being represented by x_i, y_i, z_i ; the significance of $dp_1 \cdots dp_{3N}$ is analogous, the corresponding momenta being involved. It should be noted that the factor $1/N!$ has been introduced in equation (67.1) to allow for the indistinguishability of the particles; in other words, the particles are not localized elements, the whole of the volume being available to all of them. Since the particles interact weakly only, the energy represented in the Hamiltonian form by $H(p, q)$ is purely kinetic in character; hence, for the system of N molecules

$$H(p, q) = \frac{1}{2m} \sum_{i=1}^N (p_x^2 + p_y^2 + p_z^2)_i. \quad (67.2)$$

Since the molecules are independent, it is possible to integrate over the variables in equation (67.1) in turn, and by comparison with Section 57b, the result can be readily seen to be

$$Q_e = \frac{1}{N!} \left\{ \frac{(2\pi mkT)^{3/2}}{h^3} V \right\}^N, \quad (67.3)$$

where V is the total volume of the system. It will be noted that the expression in the brackets, i.e., $(2\pi mkT)^{3/2} V/h^3$, is the translational partition function Q_t for a single molecule, as given by equation (57.5).

In the evaluation of the partition function Q_i for internal degrees of freedom of the N particles, the latter may be treated as localized (distinguishable) elements (cf. Section 58f); this contribution is thus seen to be equal to

Q_i^N , where Q_i is the internal partition function for a single molecule. The complete partition function for the system of N molecules is thus given by

$$\begin{aligned} Q &= Q_i Q_i \\ &= \frac{1}{N!} \left\{ \frac{(2\pi mkT)^{3/2}}{h^3} V \right\}^N Q_i^N \\ &= \frac{1}{N!} Q^N, \end{aligned} \quad (67.4)$$

where Q , equal to $Q_i Q_i$, is the complete partition function for a *single* molecule. It follows, therefore, that the equations of the preceding chapter, giving the various thermodynamic properties in terms of the partition function for a single molecule, may now be modified by using the partition function Q for the whole system. By combining equation (56.11) with (67.4), it is seen that

$$A = -kT \ln Q, \quad (67.5)$$

and from this it follows that

$$P = - \left(\frac{\partial A}{\partial V} \right)_T = kT \left(\frac{\partial \ln Q}{\partial V} \right)_T. \quad (67.6)$$

Since the internal contribution to the partition function is independent of the volume, equation (67.6) can be written in the form

$$P = kT \left(\frac{\partial \ln Q_i}{\partial V} \right)_T. \quad (67.7)$$

The expressions for other thermodynamic functions in terms of Q may be readily derived; thus,

$$\begin{aligned} F &= A + PV \\ &= kT \left\{ -\ln Q + V \left(\frac{\partial \ln Q}{\partial V} \right)_T \right\}, \end{aligned} \quad (67.8)$$

and

$$S = - \left(\frac{\partial A}{\partial T} \right)_V = k \left\{ \ln Q + T \left(\frac{\partial \ln Q}{\partial T} \right)_V \right\}. \quad (67.9)$$

Further,

$$\begin{aligned} E &= A + TS \\ &= kT^2 \left(\frac{\partial \ln Q}{\partial T} \right)_V. \end{aligned} \quad (67.10)$$

Although the foregoing equations have been derived for the special case of a system of weakly interacting particles, they are actually of quite general applicability. It can be shown by the methods of Section 56d, that provided the complete partition function Q is calculated properly, with due

allowance for interaction, these equations may be used to determine the thermodynamic properties of systems of dependent particles.

67c. Thermodynamics of Atomic Crystals.—A simple application of the use of the partition function for the whole system is to be found in the study of the crystalline state. A crystal may be regarded as a system of localized elements, whose energy is entirely vibrational in character. One gram atom consists of N individual atoms, each of which possesses three degrees of vibrational freedom, making a total of $3N$ vibrational modes for the system. Assuming the oscillations are simple harmonic in character, it follows that the complete partition function will be given by the product of $3N$ terms of the type $(1 - e^{-h\nu_i/kT})^{-1}$, as indicated by equation (60.3); it should be noted that the frequency ν_i is here expressed in sec^{-1} . As seen in Section 60a, this partition function is based on the lowest vibrational level as the energy zero; if the energy is expressed with reference to the actual zero, i.e., the bottom of the potential energy curve, of the oscillator, it is necessary to multiply each term by $e^{-h\nu_i/2kT}$, where $\frac{1}{2}h\nu_i$ is the zero-point energy of the particular oscillator. Inserting a factor G_0 to allow for possible degeneracy of the lowest (zero energy) level, the partition function for the whole one gram atom of crystal will be

$$Q = G_0 \prod_{i=1}^{3N} (1 - e^{-h\nu_i/kT})^{-1} e^{-h\nu_i/2kT}. \quad (67.11)$$

If all the atoms vibrated with the same frequency ν , in accordance with the Einstein theory (cf. Section 54a), this partition function would become

$$Q = G_0 (1 - e^{-h\nu/kT})^{-3N} e^{-E_0/kT}, \quad (67.12)$$

where E_0 is the total zero-point energy. At high temperatures, the partition function for a single oscillator becomes $kT/h\nu$ [cf. equation (60.9)], the classical value; under these conditions, equation (67.11) would reduce to

$$Q = G_0 \left(\frac{kT}{h\nu} \right)^{3N} e^{-E_0/kT}. \quad (67.13)$$

From equations (67.12) and (67.13) it is possible to derive the Einstein and classical expressions, respectively, for heat capacity; it is of more interest, however, to return to the complete equation (67.11) and deduce from it the Debye equation (54.19).

Upon taking logarithms of equation (67.11), viz.,

$$\ln Q = \ln G_0 - \sum_{i=1}^{3N} \ln (1 - e^{-h\nu_i/kT}) - \sum_{i=1}^{3N} \frac{h\nu_i}{2kT},$$

and combining with equation (67.10), the total energy is given by

$$E = kT^2 \left(\frac{\partial \ln Q}{\partial T} \right)_V = \sum_{i=1}^{3N} \left(\frac{h\nu_i}{e^{h\nu_i/kT} - 1} + \frac{h\nu_i}{2} \right). \quad (67.14)$$

Replacing summation by integration, this becomes

$$E = \int_1^{3N} \left(\frac{h\nu}{e^{h\nu/kT} - 1} + \frac{h\nu}{2} \right) dn,$$

and if equation (54.14) is used to change the variable, the result is

$$E = \frac{9N}{\nu_m^3} \int_0^{\nu_m} \left(\frac{h\nu}{e^{h\nu/kT} - 1} + \frac{h\nu}{2} \right) \nu^2 d\nu. \quad (67.15)$$

This is seen to be identical with equation (54.15) of the Debye treatment. From this, the Debye equations (54.20) and (54.21) for the energy and heat capacity, respectively, can, of course, be derived as shown in Section 54b.

The entropy of one gram atom of a crystal can also be obtained from the partition function, by using equation (67.9); in the present case, combination with the definition of Q , according to equation (67.11), gives

$$S = k \ln G_0 + \sum_{i=1}^{3N} \left\{ \frac{1}{e^{h\nu_i/kT} - 1} \cdot \frac{h\nu_i}{T} - k \ln (1 - e^{-h\nu_i/kT}) \right\}. \quad (67.16)$$

It will be observed that the zero-point factor disappears from this expression for the entropy, in agreement with expectation. On replacing the summation in equation (67.16) by integration, and changing the variable, as before, it is found that

$$S = k \ln G_0 + \frac{9N}{\nu_m^3} \int_0^{\nu_m} \frac{1}{e^{h\nu/kT} - 1} \cdot \frac{h\nu^3}{T} d\nu - \frac{9Nk}{\nu_m^3} \int_0^{\nu_m} \ln (1 - e^{-h\nu/kT}) \nu^2 d\nu. \quad (67.17)$$

Introduction of the quantities θ , i.e., $h\nu_m/k$, and x , i.e., $h\nu/kT$, as defined by equations (54.16) and (54.17), then yields the result

$$S = k \ln G_0 + 9Nk \left(\frac{T}{\theta} \right)^3 \left\{ \int_0^{\theta/T} \frac{x^3}{e^x - 1} dx - \int_0^{\theta/T} \ln (1 - e^{-x}) x^2 dx \right\}. \quad (67.18)$$

The second integral in equation (67.18) may be integrated by parts; thus,

$$\begin{aligned} 9Nk \left(\frac{T}{\theta} \right)^3 \int_0^{\theta/T} \ln (1 - e^{-x}) x^2 dx \\ = 3Nk \left\{ \ln (1 - e^{-\theta/T}) - \left(\frac{T}{\theta} \right)^3 \int_0^{\theta/T} \frac{x^3}{e^x - 1} dx \right\}, \end{aligned}$$

so that equation (67.18) becomes

$$S = k \ln G_0 + 12Nk \left(\frac{T}{\theta} \right)^3 \int_0^{\theta/T} \frac{x^3}{e^x - 1} dx - 3Nk \ln (1 - e^{-\theta/T}). \quad (67.19)$$

The remaining integral in equation (67.19) may be evaluated by the methods described in Section 54b; at low temperatures, in particular, the expression

for the entropy reduces to the form

$$S = k \ln G_0 + Nk \left\{ \frac{4}{5} \pi^4 \left(\frac{T}{\theta} \right)^3 - \dots \right\}. \quad (67.20)$$

It will be observed that at the absolute zero of temperature, i.e., $T = 0$, the entropy S_0 of a simple crystal is given by

$$S_0 = k \ln G_0, \quad (67.21)$$

where G_0 is the degeneracy, or statistical weight, of the state of zero energy. If G_0 is unity, that is to say, there is only one eigenstate, then the entropy at 0°K will be zero, as required by the third law of thermodynamics. If, however, for any reason, the crystal exhibits a degeneracy in the state of zero energy, the entropy cannot be zero at the absolute zero, and the third law will appear to fail. Illustrations of this type of behavior have already been referred to in Section 63a.

67d. Partition Function for System of Dependent Particles.—For a system of N dependent particles which are not localized, the partition function for the external coordinates is still given by equation (67.1), but the energy is now not merely kinetic energy of translation; it must include the potential energy of interaction. The Hamiltonian expression for the (external) energy is thus

$$H(p, q) = \frac{1}{2m} \sum_{i=1}^N (p_x^2 + p_y^2 + p_z^2)_i + U(q), \quad (67.22)$$

where $U(q)$, the potential energy of the whole system of N molecules, is a function of the $3N$ positional coordinates. If this result is introduced into equation (67.1), it is possible, as before, to carry out the integration over the momenta, which are independent, but not over the coordinates, since the value of the function $U(q)$ is not known. The result is consequently

$$Q_e = \frac{1}{N!} \left\{ \frac{(2\pi mkT)^{3/2}}{h^3} \right\}^N \int \dots \int e^{-U(q)/kT} dq_1 \dots dq_{3N}, \quad (67.23)$$

in which expression the portion involving the integrals is sometimes referred to as the *configuration integral*. If the latter is represented by the symbol Q_u , then

$$Q_u = \int \dots \int e^{-U(q)/kT} dq_1 \dots dq_{3N} \quad (67.24)$$

and

$$Q_e = \frac{1}{N!} \left\{ \frac{(2\pi mkT)^{3/2}}{h^3} \right\}^N Q_u. \quad (67.25)$$

It will be seen that the quantity in the brackets in equations (67.23) and (67.25) is the translational partition function for a single molecule, with the omission of the volume V . For a perfect gas, when the molecules do not

attract one another, $U(q)$ is zero, and hence the configuration integral, equation (67.24), becomes equal to V^N , thus supplying the missing factor. However, for real gases, $U(q)$ is not zero, and the value of the configuration integral must differ from V^N ; it will, nevertheless, always be a function of the volume of the system.

In the foregoing treatment the contributions of the external and internal degrees of freedom to the complete partition function of the system have been regarded as independent, and examination of equation (67.23) or (67.25) shows that a further separation is possible. It is seen that the two factors making up the partition function Q , for the external coordinates, are due to kinetic and potential energies, respectively. The former is identical with that for an ideal gas, with the omission of the volume V but the inclusion of $1/N!$, while the latter is given by the configuration integral. It is seen, therefore, that this integral may be regarded as the contribution to the complete partition function of the system of the potential energy of interaction of the N particles.

67e. Evaluation of the Configuration Integral.—There are several methods, of varying degrees of approximation, by means of which it is possible to obtain a more useful expression for the configuration integral. The most accurate are very complicated, but a similar result can be obtained by means of other, less rigid, procedures, due to the cancellation of errors. The following simplified, but inexact, treatment indicates one type of argument that has been employed. It is supposed that the total potential energy $U(q)$ can be represented as the sum of the interactions $u(r_{ij})$ between all possible pairs of molecules i and j , depending only on their distance apart r_{ij} ; thus,

$$U(q) = \sum_{ij} u(r_{ij}). \quad (67.26)$$

This assumption implies that the potential energy of a group of three adjacent molecules is equal to the sum of the energies for the three equivalent pairs treated as independent. For example, if there is a cluster of three molecules designated by a , b and c , the total energy of the group is assumed to be equal to the sum of the values for the separate pairs ab , bc and ac . The same idea is extended to any aggregation of molecules; in each case the potential energy is regarded as equal to the sum of the energies for all possible pairs that can be formed by the molecules in that aggregation.

Using the approximation represented by equation (67.26), the expression for the configuration integral may be written as

$$Q_u = \int \cdots \int e^{-\sum_{ij} u(r_{ij})/kT} dx_1 dy_1 dz_1 \cdots dx_N dy_N dz_N, \quad (67.27)$$

and one possible way of evaluating the integral is to carry out the integration over the coordinates of each molecule in turn. Starting with the molecule indicated by the subscript N , the expression for the potential energy may

be divided into two parts, viz.,

$$\sum_{ij} u(r_{ij}) = \sum_{ij \neq N} u(r_{ij}) + \sum_{i \neq N} u(r_{iN}), \quad (67.28)$$

in which the first represents the interaction energy of all pairs not including the N th molecule, while the second gives the potential energy for the interaction of this molecule with each of the others in turn. Since the former is independent of the coordinates of the N th molecule, it follows that integration over the coordinates x_N, y_N, z_N , in equation (67.27) gives

$$I_N = \int \int \int e^{-\sum_{i \neq N} u(r_{iN})/kT} dx_N dy_N dz_N. \quad (67.29)$$

It is, of course, possible to write

$$e^{-\sum_{i \neq N} u(r_{iN})/kT} = \prod_{i \neq N} e^{-u(r_{iN})/kT},$$

and if a function $f(r_{ij})$ or, in brief, f_{ij} , is defined by

$$f(r_{ij}) = f_{ij} = e^{-u(r_{ij})/kT} - 1, \quad (67.30)$$

then

$$e^{-u(r_{iN})/kT} = 1 + f_{iN}. \quad (67.31)$$

Introduction of this result into equation (67.30), gives

$$\begin{aligned} e^{-\sum_{i \neq N} u(r_{iN})/kT} &= \prod_{i \neq N} (1 + f_{iN}) \\ &= 1 + \sum_{i \neq N} f_{iN} + \dots, \end{aligned} \quad (67.32)$$

where equation (67.32) is the result of the expansion of the product, all terms beyond the second being neglected. Utilizing this result, equation (67.29) becomes

$$I_N = \int \int \int dx_N dy_N dz_N + \int \int \int \sum_{i \neq N} f_{iN} dx_N dy_N dz_N,$$

in which the first integral is equal to V , the volume of the containing vessel; hence, using equation (67.31) to eliminate f_{iN} , it follows that

$$I_N = V + \int \int \int \sum_{i \neq N} \{e^{-u(r_{iN})/kT} - 1\} dx_N dy_N dz_N. \quad (67.33)$$

For a system of particles which do not interact to any appreciable extent, the remaining integral would, of course, be zero; integration of the configuration integral over the coordinates of each of the particles then gives V only, in each case, and for all N particles the result would be V^N , as stated above.

In general, the integral in equation (67.33) is equal to the sum of $N - 1$ identical terms of the type of

$$\iiint \{e^{-u(r_{iN})/kT} - 1\} dx_N dy_N dz_N = \beta,$$

so that, by equation (67.33),

$$I_N = V + (N - 1)\beta, \quad (67.34)$$

where $u(r_{iN})$ is the potential energy of interaction between the N th molecule and any one of the remaining $N - 1$ molecules.

Actually the integral represented by β will be the same for any pair of molecules, which are assumed to be of the same species, and so it is possible to write

$$\beta = \iiint \{e^{-u(r_{ij})/kT} - 1\} dx_j dy_j dz_j, \quad (67.35)$$

in which $u(r_{ij})$ is now the potential energy for any pair of molecules, ij , as a function of their distance apart, r_{ij} . In order to simplify this integral, the position of the molecule i may be taken as the origin of spherical coordinates, so that

$$\beta = \iiint \{e^{-u(r)/kT} - 1\} r^2 \sin \theta d\phi d\theta dr. \quad (67.36)$$

The integration limits should be determined by the size of the containing vessel, but since the interaction forces between molecules fall off very rapidly with increasing distance, the integration may be carried out over r from zero to infinity, and over all values of the angles θ and ϕ . The quantity $e^{-u(r)/kT} - 1$ falls off so rapidly with increasing r , that extension of the integration to infinity makes no appreciable difference to the result. Integration over the angles gives 4π , and so

$$\beta = 4\pi \int_0^\infty \{e^{-u(r)/kT} - 1\} r^2 dr, \quad (67.37)$$

and, as noted above, this has the same form for any pair of molecules.

It can be readily seen from the foregoing arguments that while integration of the configuration integral over the coordinates of the N th molecule gives I_N , as represented by equation (67.34), integration over the coordinates of the $(N - 1)$ th molecule will give

$$I_{N-1} = V + (N - 2)\beta,$$

since there are now $N - 2$ interacting pairs, the interaction of the molecules $N - 1$ and N having already been included in I_N . Similarly, integration

over the coordinates of the $(N - 2)$ th molecule gives

$$I_{N-2} = V + (N - 3)\beta,$$

and so on. The configuration integral is equal to the product of the N separate integrals over the coordinates of the individual molecules; hence

$$\begin{aligned} Q_u &= I_N I_{N-1} I_{N-2} \cdots I_1 \\ &= \{V + (N - 1)\beta\} \{V + (N - 2)\beta\} \cdots V \\ &= V^N \left\{ 1 + (N - 1) \frac{\beta}{V} \right\} \left\{ 1 + (N - 2) \frac{\beta}{V} \right\} \cdots 1 \\ &\approx V^N \left\{ 1 + \frac{1}{2} N^2 \frac{\beta}{V} + \cdots \right\}, \end{aligned} \quad (67.38)$$

where $\frac{1}{2}N(N - 1)$ has been taken as equal to $\frac{1}{2}N^2$, since N is large, and all terms beyond the second in the expansion of the product have been neglected.

For the purpose of determining the contribution of the configuration integral to the thermodynamic functions of the system, it is desirable to know the value of $\ln Q_u$, rather than of Q_u itself; hence, from equation (67.38),

$$\ln Q_u = N \ln V + \ln \left(1 + \frac{1}{2} N^2 \frac{\beta}{V} + \cdots \right). \quad (67.39)$$

The approximation is now made of treating $\frac{1}{2}N^2\beta/V$ as small; this is justifiable when the integral β is small, as it will be for slightly imperfect gases in which the molecular interaction is not large, or when N/V is small, that is, for low gas pressures. In these circumstances

$$\ln \left(1 + \frac{1}{2} N^2 \frac{\beta}{V} + \cdots \right) \approx \frac{1}{2} N^2 \frac{\beta}{V},$$

and hence,

$$\ln Q_u = N \ln V + \frac{1}{2} N^2 \frac{\beta}{V}. \quad (67.40)$$

Introducing the value of β given by equation (67.36), this becomes

$$\ln Q_u = N \ln V + 2\pi \frac{N^2}{V} \int_0^\infty \{e^{-u(r)/kT} - 1\} r^2 dr. \quad (67.41)$$

Since an almost identical expression for $\ln Q_u$ can be obtained by much more precise methods than that given here, the result will be adopted for subsequent discussion; as just indicated, it is particularly applicable under conditions of slight gas imperfection.

THE IMPERFECT GAS

68a. Pressure of Imperfect Gas.—According to equation (67.7), the pressure of a gas may be expressed in terms of the external partition function Q_e , by

$$P = kT \left(\frac{\partial \ln Q_e}{\partial V} \right)_T,$$

and since, by equation (67.25), Q_u is the only part of Q_e that is dependent on the volume, it follows that

$$P = kT \left(\frac{\partial \ln Q_u}{\partial V} \right)_T. \quad (68.1)$$

Hence, utilizing equation (67.40),

$$\begin{aligned} P &= \frac{NkT}{V} - \frac{1}{2}\beta \frac{N^2 kT}{V^2} \\ &= \frac{NkT}{V} \left(1 - \frac{1}{2}\beta \frac{N}{V} \right). \end{aligned} \quad (68.2)$$

This is the general equation of state of a gas to the approximation that equation (67.40) is applicable, that is, under conditions of a fairly small degree of gas imperfection. It is apparent that when there are no intermolecular forces, β is zero, and equation (68.2) reduces to the ideal gas law, $P = NkT/V$.

The equation of state of a gas is frequently written in the so-called *virial form*, viz.,

$$P = \frac{NkT}{V} \left\{ 1 + \frac{B(T)}{V} + \frac{C(T)}{V^2} + \dots \right\},$$

where $B(T)$, $C(T)$, etc., which are functions of temperature, are known as the second, third, etc., virial coefficients. At moderate pressures, that is, for a slight gas imperfection, the terms $C(T)/V^2$ and beyond in the virial equation may be neglected, so that

$$P = \frac{NkT}{V} \left\{ 1 + \frac{B(T)}{V} \right\}. \quad (68.3)$$

This expression should hold under the same conditions as equation (68.2), and so it is possible to identify the second virial coefficient as

$$B(T) = - \frac{1}{2}\beta N \quad (68.4)$$

$$= - 2\pi N \int \{ e^{-u(r)/kT} - 1 \} r^2 dr. \quad (68.5)$$

68b. Free Energy and Fugacity of Imperfect Gases.—The general expression for the free energy F , which is equal to $A + PV$, is given by equation (67.5), as

$$\begin{aligned} F &= -kT \ln Q + PV \\ &= -kT \ln Q_u Q_i + PV. \end{aligned} \quad (68.6)$$

At extremely low pressures, when the gas may be regarded as behaving ideally, equation (68.6) may be written in the form

$$F^* = -kT \ln \left\{ \frac{1}{N!} \cdot \frac{(2\pi mkT)^{3/2}}{h^3} V^* \right\}^N Q_i + NkT,$$

an asterisk being employed to indicate the low pressure state. For a real gas,

$$F = -kT \ln \left\{ \frac{1}{N!} \cdot \frac{(2\pi mkT)^{3/2}}{h^3} \right\}^N Q_u Q_i + PV,$$

so that

$$F - F^* = -kT(\ln Q_u - N \ln V^*) + PV - NkT.$$

Introduction of the expression for $\ln Q_u$, from equation (67.40), then yields

$$F - F^* = -NkT \left(\frac{1}{2}\beta \frac{N}{V} + \ln \frac{V}{V^*} + 1 \right) + PV. \quad (68.7)$$

The *fugacity* f of a gas may be defined in terms of the free energies as

$$F - F^* = NkT \ln \frac{f}{f^*},$$

and hence, by equation (68.7),

$$\begin{aligned} NkT \ln \frac{f}{f^*} &= -NkT \left(\frac{1}{2}\beta \frac{N}{V} + \ln \frac{V}{V^*} + 1 \right) + PV, \\ \therefore \ln \frac{f}{f^*} &= - \left(\frac{1}{2}\beta \frac{N}{V} + \ln \frac{V}{V^*} + 1 \right) + \frac{PV}{NkT}. \end{aligned}$$

Since f^* is the fugacity at very low pressure, it may be replaced by the pressure, and hence by NkT/V^* , since the gas then approximates to ideal behavior, so that

$$\ln f = -\frac{1}{2}\beta \frac{N}{V} + \ln \frac{NkT}{V} + \frac{PV}{NkT} - 1.$$

Utilizing the value of PV/NkT according to equation (68.2), this becomes

$$\ln f = -\beta \frac{N}{V} + \ln \frac{NkT}{V}, \quad (68.8)$$

and since $\beta N/V$ is small, it follows that

$$f = \frac{NkT}{V} \left(1 - \beta \frac{N}{V} \right). \quad (68.9)$$

For practical purposes, equations (68.8) and (68.9) may be written as

$$\ln f = \frac{2B(T)}{V} + \ln \frac{NkT}{V} \quad (68.10)$$

and

$$f = \frac{NkT}{V} \left\{ 1 + \frac{2B(T)}{V} \right\}. \quad (68.11)$$

It is possible, by means of equations (68.2) and (68.9) to derive a relationship between the fugacity and the pressure, first developed in another manner by Lewis and Randall.⁶ It follows from equation (68.2), neglecting the term containing β^2 , that

$$P^2 = \left(\frac{NkT}{V} \right)^2 \left(1 - \beta \frac{N}{V} \right).$$

The quantity NkT/V is the pressure an ideal gas would exert if N molecules occupied the volume V ; this is called the *ideal pressure* P_i , and hence

$$P^2 = P_i^2 \left(1 - \beta \frac{N}{V} \right). \quad (68.12)$$

Similarly, from equation (68.9),

$$f = P_i \left(1 - \beta \frac{N}{V} \right), \quad (68.13)$$

and consequently, from equations (68.12) and (68.13),

$$f = \frac{P^2}{P_i}. \quad (68.14)$$

68c. The van der Waals Gas.—The use of a simple model, in conjunction with the relationship already derived between the integral β and the second virial coefficient, permits of the derivation of an equation of state which is identical with the van der Waals equation at low pressures. According to the proposed model, molecules act as completely impenetrable spheres of diameter r_0 ; that is to say, two molecules will attract each other according to a definite law as long as the distance between their centers is greater than r_0 , but at the intermolecular distance r_0 the attraction ceases and is replaced by an infinite repulsion. The form of the potential energy curve

⁶ Lewis and Randall, "Thermodynamics," p. 198.

for the postulated model is shown in Fig. 46. In these circumstances the integral β can be divided into two parts; one between the limits of zero and r_0 , in which the potential term $u(r)$ is infinite, so that $e^{-u(r)/kT} - 1$ is equal to -1 , and the other between r_0 and infinity, viz.,

$$\beta = -4\pi \int_0^{r_0} r^2 dr + 4\pi \int_{r_0}^{\infty} \{e^{-u(r)/kT} - 1\} r^2 dr. \quad (68.15)$$

The first integral is clearly equal to $\frac{4}{3}\pi r_0^3$, and the second may be simplified by assuming $u(r)$ to be small (numerically) in comparison with kT , so that

$$e^{-u(r)/kT} - 1 \approx \frac{-u(r)}{kT},$$

and hence

$$\beta = -\frac{4}{3}\pi r_0^3 - \frac{4\pi}{kT} \int_{r_0}^{\infty} u(r) r^2 dr. \quad (68.16)$$

According to equation (68.4), the second virial coefficient is equal to $-\frac{1}{2}\beta N$, and hence,

$$B(T) = \frac{2}{3}N\pi r_0^3 + \frac{2\pi N}{kT} \int_{r_0}^{\infty} u(r) r^2 dr. \quad (68.17)$$

If N is taken as the Avogadro number, so that the system under consideration consists of one mole of gas, equation (68.17) may be written in the form

$$B(T) = b - \frac{a}{RT}, \quad (68.18)$$

where b and a are defined by

$$b = \frac{2}{3}N\pi r_0^3 \quad (68.19)$$

and

$$a = -2\pi N^2 \int_{r_0}^{\infty} u(r) r^2 dr. \quad (68.20)$$

Since r_0 is the effective (collision) diameter of a single molecule, the volume will be $\frac{4}{3}\pi r_0^3$, assuming it to be spherical, and hence b , as given by equation (68.19), is seen to be equal to four times the actual volume of the N molecules. Further, since $u(r)$ is the interaction energy between two

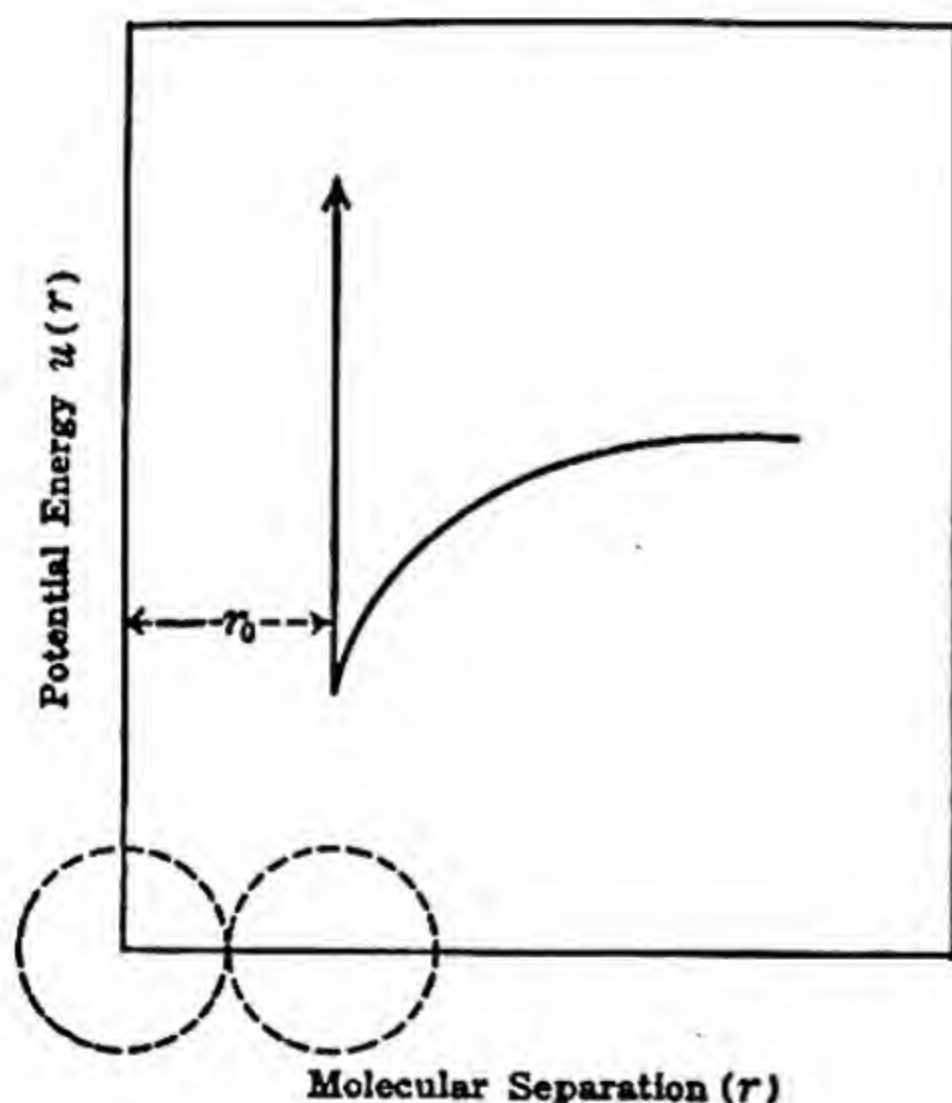


FIG. 46. Potential function for van der Waals gas

molecules, it appears, in view of the negative sign, that the quantity a is a measure of the molecular attractive force. It is evident, therefore, that a

and b as defined above are equivalent to the van der Waals constants a and b , which have, in fact, the significance just given. Utilizing the simplified equation of state (68.3), for one mole of gas, namely

$$P = \frac{RT}{V} \left\{ 1 + \frac{B(T)}{V} \right\},$$

and the value of $B(T)$ given by equation (68.18), then

$$P = \frac{RT}{V} \left\{ 1 + \frac{1}{V} \left(b - \frac{a}{RT} \right) \right\},$$

$$\therefore PV = RT \left\{ 1 + \frac{1}{V} \left(b - \frac{a}{RT} \right) \right\}. \quad (68.21)$$

Although it is not immediately evident that this expression is virtually identical with the van der Waals equation, the connection can be best shown by starting with the latter, viz.,

$$\left(P + \frac{a}{V^2} \right) (V - b) = RT,$$

and rewriting it in the form

$$PV = RT + b \left(P + \frac{a}{V^2} \right) - \frac{a}{V}$$

$$= RT + \frac{bRT}{V - b} - \frac{a}{V}.$$

If the approximation is made of writing V for $V - b$ in the denominator of the second term on the right-hand side, it follows that

$$PV = RT + \frac{bRT}{V} - \frac{a}{V},$$

which is identical with equation (68.21). It is seen, therefore, that the van der Waals equation may be expected to hold, for the particular model, under such conditions that virial coefficients beyond the second may be ignored in the general equation of state, i.e., under conditions of moderately small gas imperfection.

By the use of the expression for the attractive (dispersion) forces derived in Section 66c, it is possible to carry further the calculations relating to the van der Waals equation. Neglecting the repulsive forces, the potential function $u(r)$ may be taken as equal to the interaction energy given by equation (66.21); hence the van der Waals constant a can be written

as

$$\begin{aligned}
 a &= -2\pi N^2 \int_{r_0}^{\infty} u(r) r^2 dr \\
 &= \frac{3}{2} \pi N^2 h \nu_0 \alpha^2 \int_{r_0}^{\infty} \frac{1}{r^4} dr \\
 &= \frac{1}{2} \pi N^2 h \frac{\nu_0 \alpha^2}{r_0^3}.
 \end{aligned} \tag{68.22}$$

Apart from the universal constants, the value of a is seen to depend on ν_0 , α and r_0 , all of which are known, at least approximately, for a number of gases. It is thus possible to calculate the magnitude of the van der Waals constant a directly, but a more convenient test is to introduce the expression for b , according to equation (68.19), and thus to eliminate r_0^3 ; it is then found that

$$ab = \frac{1}{3} \pi^2 N^3 h \nu_0 \alpha^2.$$

If the value of b is known, it should be possible to calculate a and to compare it with that derived experimentally; this comparison of the a 's, in atm. cc.² g.⁻² units, for a number of gases is made in Table XXIII. The satisfactory

TABLE XXIII. EXPERIMENTAL AND CALCULATED VAN DER WAALS CONSTANT

Gas	a (Calc.)	a (Obs.)
He	4.8	3.5
Ne	26	21
A	163	135
H ₂	46	24.5
N ₂	147	135
Cl ₂	680	632
CO ₂	334	361

agreement may be regarded as confirming the general accuracy of the identification of the dispersion forces with the van der Waals attraction.

69a. Generalized Model of Imperfect Gas.⁷—In the simple molecular model treated in the preceding section, the repulsive forces were neglected for all distances greater than the distance of closest approach of two molecules; at smaller distances the repulsion was supposed to be infinitely great. The problem can be treated in a more general manner by postulating a model which satisfies the bireciprocal function

$$u(r) = \frac{A}{r^n} - \frac{B}{r^m}, \tag{69.1}$$

as derived in Section 66d, for the mutual interaction (potential) energy of two molecules. The first term on the right-hand side represents the contri-

⁷ Lennard-Jones, *Proc. Roy. Soc., A*, 106, 463 (1924); *Physica*, 4, 941 (1937); see also, de Boer and Michels, *Physica*, 5, 945 (1938).

bution of the repulsive forces, while the second term, with the negative sign, is due to the mutual attraction of the molecules. As can be readily shown, n must be greater than m , in order that there may be a resultant attraction at relatively large distances and repulsion at very small distances of separation. The general nature of the potential function is illustrated in Fig. 47; curve A indicates the type of plot for the repulsive term A/r^n , while B shows the character of the attractive $-B/r^m$ term. The resultant of the two terms is given by the full line; it is seen that when two molecules are brought together from infinity, the attraction increases, as implied by the decreasing potential energy. The latter passes through a minimum, which represents the equilibrium state of the system, then at closer distances of approach there is rapidly increasing repulsion. If the two molecules do not interact chemically, the depth of the potential energy at the minimum is of the order of 5 kcal. per mole below that for infinite separation; this is the order of magnitude of van der Waals forces. The potential function (69.1) may be written in the alternative form

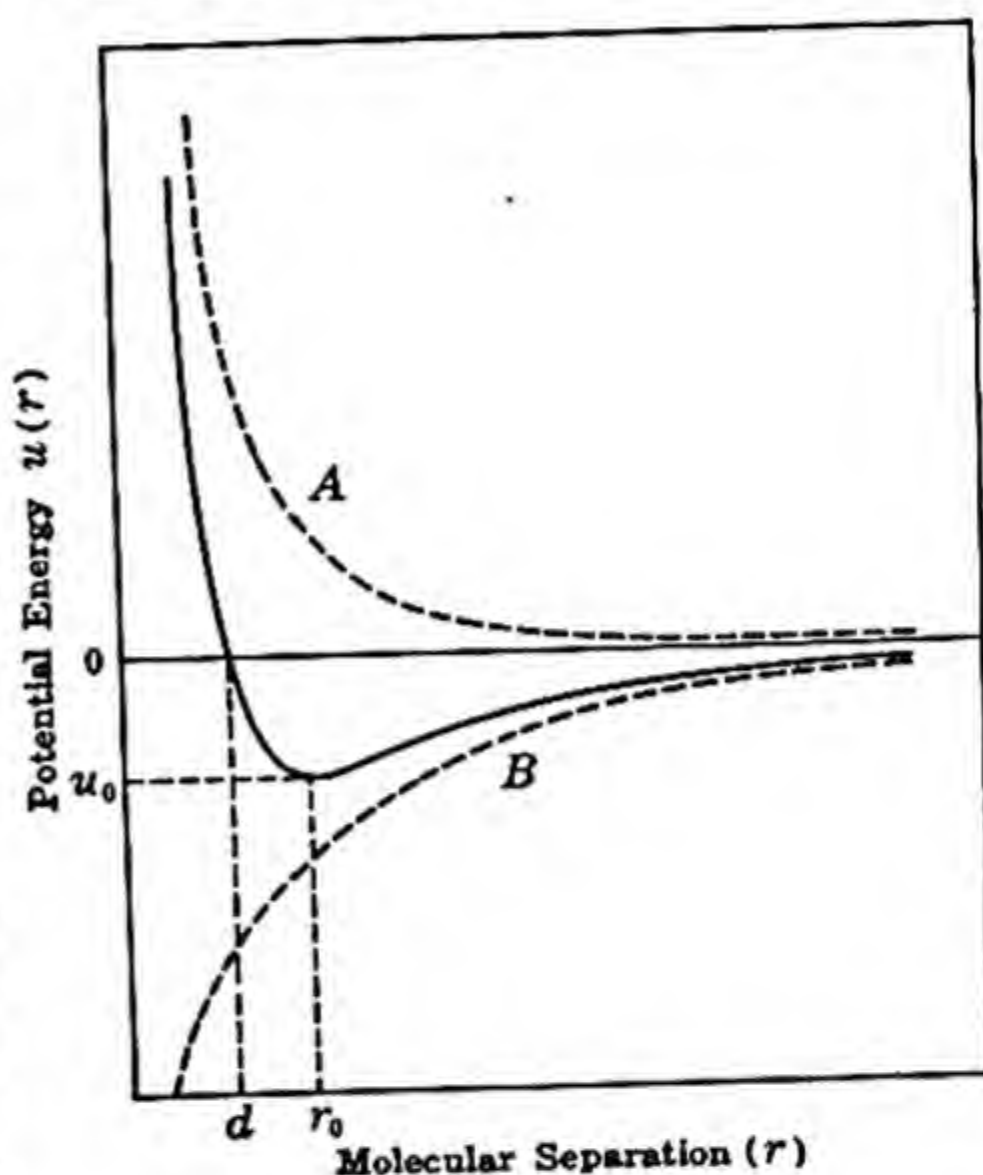


FIG. 47. Attractive and repulsive forces between molecules

$$u(r) = u_0 \left\{ \frac{n}{n-m} \left(\frac{r_0}{r} \right)^m - \frac{m}{n-m} \left(\frac{r_0}{r} \right)^n \right\}, \quad (69.2)$$

where the constants A and B of equation (69.1) are related to u_0 and r_0 of equation (69.2) by

$$A = -u_0 \frac{m}{n-m} r_0^n \quad \text{and} \quad B = -u_0 \frac{n}{n-m} r_0^m, \quad (69.3)$$

therefore,

$$\frac{A}{B} = \frac{m}{n} r_0^{n-m}. \quad (69.4)$$

The physical significance of r_0 and u_0 may be readily seen by differentiating equation (69.2) with respect to r , and equating the result to zero; it is found that r is then equal to r_0 , and hence u is equal to u_0 . It follows, therefore, that r_0 must represent the distance between the centers of two molecules at the minimum of the potential energy curve, and u_0 is the corresponding value of the potential energy.

It is apparent that there are two points at which the potential energy is zero; one is when the two molecules are infinitely far apart, i.e., when r is infinite, and the other is that when attractive and repulsive forces become equal. This second point is of interest because the corresponding intermolecular distance may be regarded as a measure of the effective collision diameter of the molecule; if this distance is represented by d , then it follows from equation (69.2) that

$$\frac{n}{n-m} \left(\frac{r_0}{d} \right)^m = \frac{m}{n-m} \left(\frac{r_0}{d} \right)^n, \\ \therefore d = r_0 \left(\frac{m}{n} \right)^{1/(n-m)}. \quad (69.5)$$

The second virial coefficient $B(T)$ for a moderately imperfect gas is given by equation (68.5) as

$$B(T) = -2\pi N \int_0^\infty \{e^{-u(r)/kT} - 1\} r^2 dr,$$

and integration by parts yields

$$B(T) = -\frac{2\pi N}{3kT} \int_0^\infty \frac{du(r)}{dr} e^{-u(r)/kT} r^3 dr. \quad (69.6)$$

(It may be observed that $-du(r)/dr$ is equal to the resultant force between two molecules.) It is now possible to insert the expression for the potential function $u(r)$, as given by equation (69.2), and to carry out the indicated integration. It may be noted, incidentally, that if the resulting value for $B(T)$ is to be finite, both m and n must be greater than 3; since n is equal to 6, according to the calculation of the dispersion forces, and m must be greater than n , the conditions for $B(T)$ to be real are satisfied.

The integration of equation (69.6) has been carried out by Lennard-Jones (1924) who found that

$$B(T) = \frac{2}{3}\pi d^3 F(y), \quad (69.7)$$

in which d is defined by equation (69.5), and $F(y)$ is a function of y , viz.,

$$F(y) = y^{3/(n-m)} \left\{ \Gamma \left(\frac{n-3}{n} \right) - 3 \sum_{c=1}^{\infty} \Gamma \left(\frac{cm-3}{n} \right) \frac{y^c}{c!} \right\}, \quad (69.8)$$

where Γ is the usual symbol for the gamma function, and y is defined by

$$y = \frac{B}{kT} \left(\frac{kT}{A} \right)^{m/n}. \quad (69.9)$$

Since y is a function of temperature only, it is evident that equation (69.7) expresses the second virial coefficient $B(T)$ as a function of the variable T . If the variation of $B(T)$ with temperature is known from experiment, as it

is for a number of gases, it should be possible, in principle, to find the values of the parameters n , m , A and B which make the calculated $B(T)$ agree with the observed result.

For reasons which will appear shortly, it is convenient to consider the plot of $\log|F(y)|$ against $\frac{n}{n-m} \log y$. In accordance with the expression previously derived for the dispersion (attractive) forces, m may be taken as 6, and the resulting $\log|F(y)|$ plotted against the corresponding $\frac{n}{n-6} \log y$, for a number of arbitrary values of y ; n is chosen as a suitable integer which, of necessity, must be greater than 6, since n is greater than m . The results obtained in this manner, from equations (69.8) and (69.9), for n equal to 8, 9, 12 and infinity, are shown in Fig. 48. It should be noted that it is the

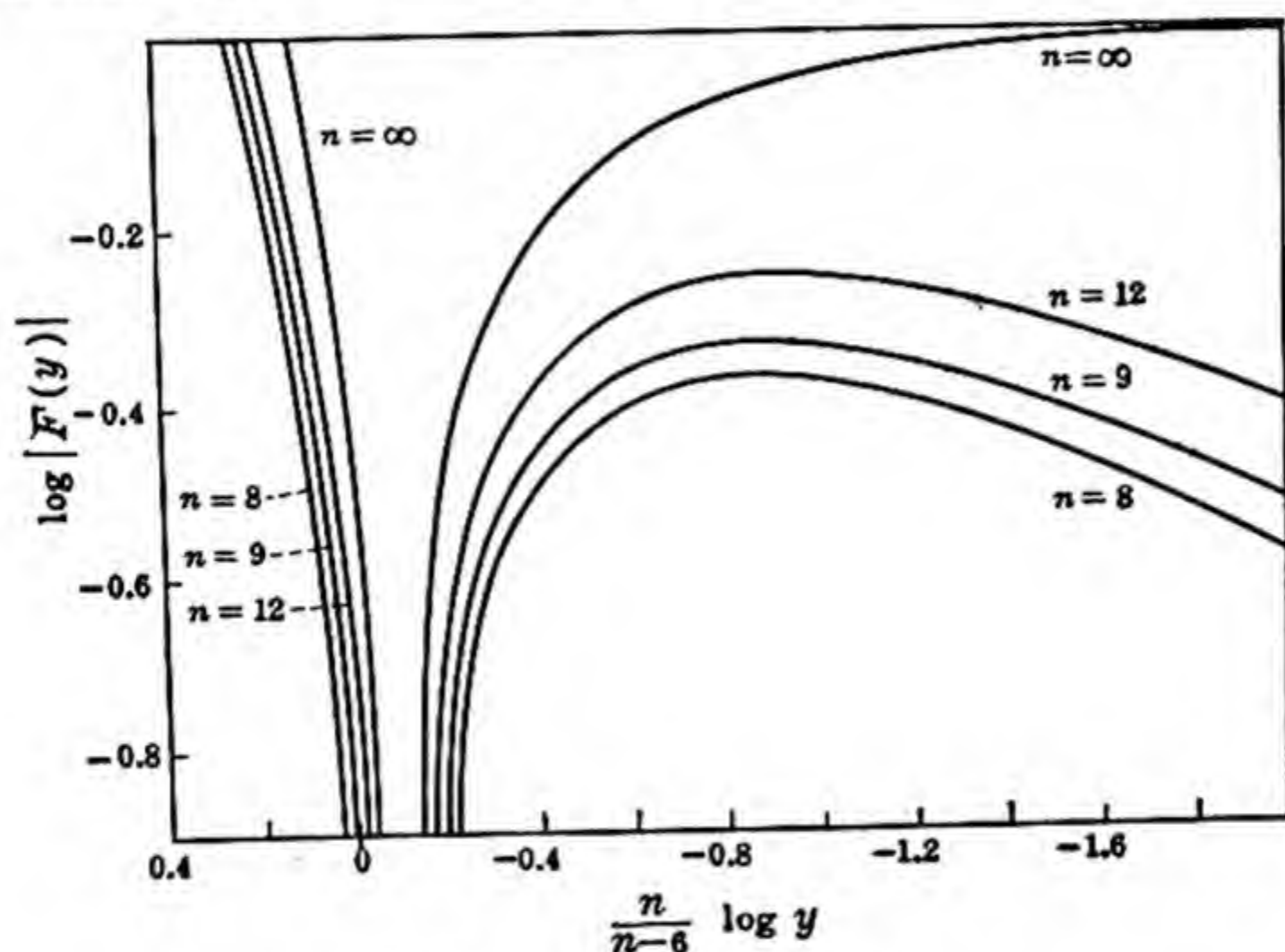


FIG. 48. Properties of imperfect gas

logarithm of the absolute value of $F(y)$, i.e., $\log|F(y)|$, that is plotted in this figure. Actually, for the curves on the left-hand side, $F(y)$ is negative, while on the right-hand side $F(y)$ is positive.

According to equation (69.7), the second virial coefficient is proportional to $F(y)$, and since n is greater than m , it follows from equation (69.9) that y is larger the lower the temperature. It is seen, therefore, according to the theoretical conclusions represented by the curves in Fig. 48, that $B(T)$ should be negative at low temperatures and should become positive at higher temperatures; this is in harmony with the experimental facts.

At a certain temperature the virial coefficient $B(T)$ is zero, and the equation of state for the gas becomes $P = NkT/V$; in other words, the gas then obeys Boyle's law and this temperature is known as the *Boyle point*, T_B . It is evident from equation (69.7) that $B(T)$ will be zero when $F(y)$ is zero, and the appropriate value of y , indicated by y_B , may be found by setting equation (69.8) equal to zero and solving for y . The results for y_B for m

equal to 6, and n equal to 9, 10, 11 and 12, are given in Table XXIV. The corresponding temperature T_B can then be calculated from equation (69.9) provided A and B are known. An alternative mode of expressing T_B is based on the fact that y is proportional to $(u_0/kT)^{(n-m)/n}$. Since n and m are known, for each case, u_0/kT_B can be calculated; the results are quoted in Table XXIV as $kT_B/|u_0|$, with the absolute value of u_0 since u_0 itself is invariably negative.

TABLE XXIV. DATA FOR THE BOYLE POINT

n	y_B	$\frac{kT_B}{ u_0 }$
9	1.140	4.58
10	1.119	4.07
11	1.110	3.71
12	1.082	3.43

Before proceeding to consider the curves of the type shown in Fig. 48 for actual gases, there is one further matter of general interest. It is seen that all the curves on the right-hand side of the figure, except that for $n = \infty$, exhibit a maximum. That is to say, if n is finite, $F(y)$, and hence the second virial coefficient, should pass through a maximum with increasing temperature. Such a maximum has actually been observed for helium at about 150°K , and neon probably has a maximum value of $B(T)$ at about 600°K . It is likely that at sufficiently high temperatures other gases would behave in an analogous manner, and hence the exponent n in equation (69.1) must be finite. This conclusion proves the approximate nature of the assumption made in the simple model of a rigid molecule considered in Section 68c, which would require n to be infinite.

It is seen from equation (69.7) that

$$\log |B(T)| = \log |F(y)| + \log \frac{2}{3} \pi d^3,$$

and from equation (69.9) that

$$\log T = \frac{n}{m-n} \log y + \frac{1}{m-n} \log \frac{A^m}{B^n} - \log k.$$

It follows, therefore, that the plot of the experimental values of $\log |B(T)|$ against $\log T$ should be superposable on the theoretical plot of $\log |F(y)|$ against $\frac{n}{n-m} \log y$, provided the postulated potential function (69.1) is reasonably satisfactory. The shape of the curve essentially determines m and n , and the change in the scale necessary to superpose the curves should permit the evaluation of A , B and d , and hence of r_0 and u_0 . In order to simplify the calculations, m is taken as 6, and then the value of n may be obtained by finding which curve in Fig. 48 best represents the plot of $\log |B(T)|$ against $\log T$ for the given gas. Unfortunately, for those gases, viz., helium, neon, argon, hydrogen and nitrogen, for which accurate experimental data for the second virial coefficient are available over a range of temperatures, an equally satisfactory fit with the $\log |F(y)|$ against $\frac{n}{n-6} \log y$ curve can be

obtained for all values of n from 8 to 14. For each value of n there are, of course, corresponding but different results for A , B , d , r_0 and u_0 . There appears to be no method available, at present, for making an unequivocal decision as to the best value of n ; however, an average value of 12 is generally taken for n , with m equal to 6, so that the potential function is written as

$$u(r) = \frac{A}{r^{12}} - \frac{B}{r^6}. \quad (69.10)$$

Using these values of m and n , the results recorded in Table XXV have been calculated from the experimental variation of $B(T)$ with temperature

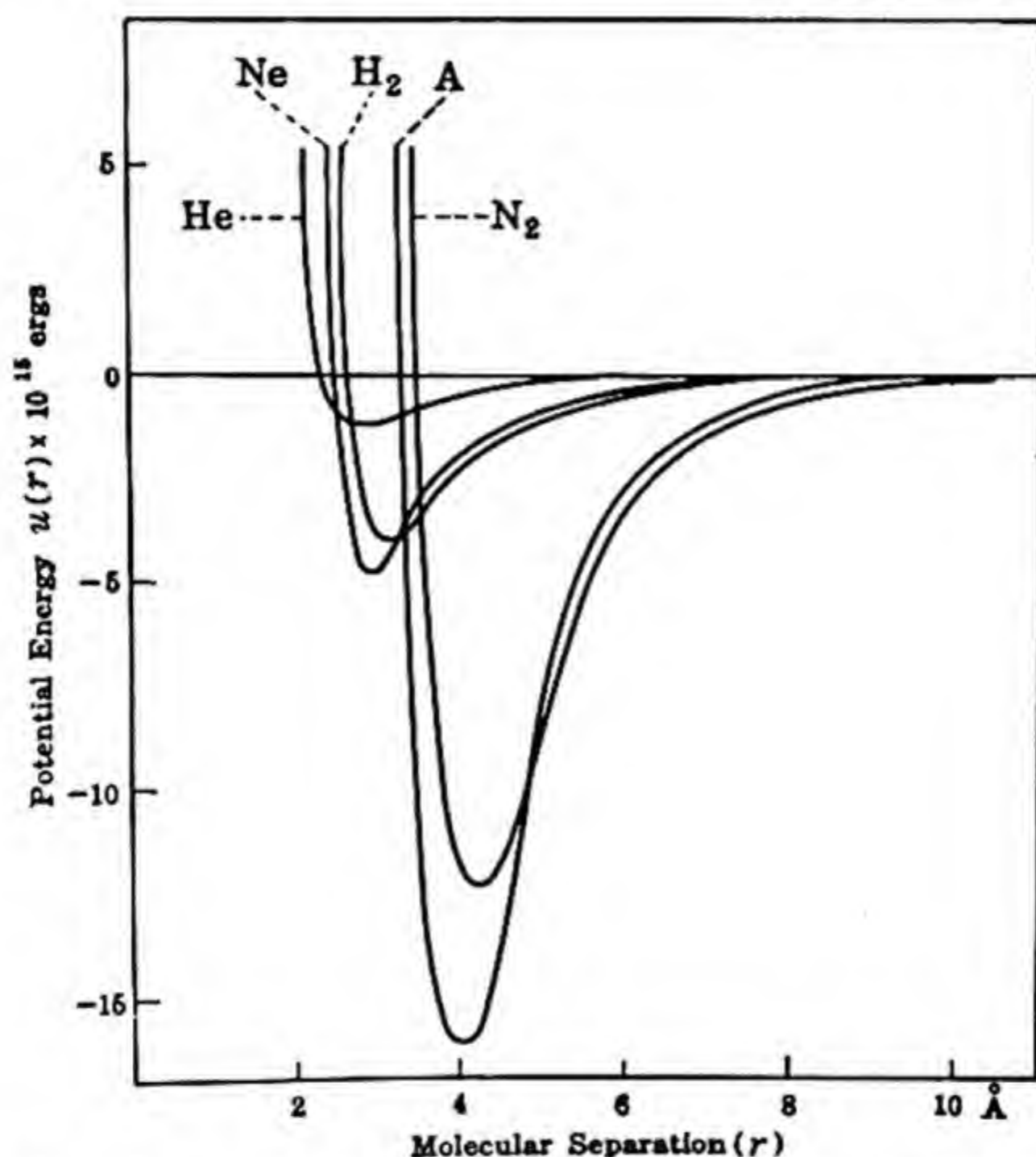


FIG. 49. Potential energy curves for interaction of molecules

for a number of gases; since u_0 is small, it is more convenient to evaluate $|u_0|/k$. All these parameters depend, of course, on the value chosen for n ; however, although A and B vary considerably with n , the important quantities d , r_0 and u_0 do not change greatly, and hence the data recorded in the table may be taken as fair averages. Utilizing the values obtained for A and B for various gases, it is possible, by means of equation (69.10), to calculate the potential energy $u(r)$ for a series of values of the intermolecular distance r ; the results for the five gases mentioned in Table XXV are plotted in Fig. 49.

Attention may be called to the fact that the use of the values of 6 and 12 for m and n , respectively, makes it possible to introduce a considerable

TABLE XXV. PROPERTIES OF GASES FROM POTENTIAL FUNCTION

Gas	$A \times 10^{10}$ (ergs Å ¹²)	$B \times 10^{10}$ (ergs Å ⁶)	d (Å)	r_0 (Å)	$ u_0 /k$ (degrees)
He	3.56	0.0108	2.63	2.95	6.03
Ne	35.5	0.0832	2.74	3.08	35.7
A	1620	1.03	3.41	3.83	120.0
H ₂	64.9	0.105	2.92	3.28	31.0
N ₂	3700	1.40	3.72	4.17	96.7

simplification in the relationships, of equations (69.3), between A , B , u_0 and r_0 ; thus, it is readily found that

$$r_0 = \left(\frac{2A}{B} \right)^{1/6} \quad \text{and} \quad |u_0| = \frac{B^2}{4A}. \quad (69.11)$$

HIGHLY COMPRESSED GASES: CONDENSATION

70a. Model of Gas Under High Pressure.—The derivation of the general equation of state (68.2), and of the van der Waals equation, which is a special case of the former, was based on the neglect of terms involving higher powers of $\beta N/V$. This approximation is equivalent to ignoring the interaction of any particular molecule with more than one other molecule at a time. In other words, the arguments are based on the assumption that encounters between molecules are never more than binary in character. This approximation is reasonably adequate to account for the behavior of gases at low densities, but it will undoubtedly fail for highly compressed gases, where encounters involving three, four or more molecules are of frequent occurrence. A direct method for the evaluation of interaction forces under these conditions has been developed, but the procedure although exact is very complicated, and does not lead to quantitative results of practical value. The treatment will be considered in Section 71, and for the present an alternative, but more approximate, approach to the problem will be examined. It has the merit of relative simplicity, and the equations derived from it are capable of direct experimental test.

The model of Lennard-Jones and Devonshire⁸ is based on the suggestion that as a result of the proximity of the molecules to one another in a highly compressed gas, each molecule may be regarded as confined to a cell (or cage). This hypothetical cell, resulting from the imprisonment of a given molecule by its immediate neighbors, may be supposed to be occupied by the molecule under consideration. Although there is a possibility that the molecule may occasionally escape from confinement, it will nevertheless spend most of its time within a cell. The significance of the migration of a molecule from one cell to another will not be considered here, but the

⁸ Lennard-Jones and Devonshire, *Proc. Roy. Soc., A*, 163, 53 (1937); 165, 1 (1938); see also, Corner, *Trans. Faraday Soc.*, 35, 711 (1939); 36, 781 (1940).

matter will be taken up more fully at a later stage. For the present purpose, however, each molecule may be regarded as the sole occupant of a cell of average volume v , equal to V/N , where V is the total volume of the highly compressed gas, and N is the number of molecules in this volume.

As each molecule moves in its cell, it will be moving in the potential fields of the surrounding molecules that really constitute the "walls" of the cell; this field will vary with time, and for purposes of calculation it must be replaced by a constant, average value. The simplest assumption to make, which will be adopted here, is that the average field in which any molecule moves is that due to its immediate neighbors when each is in its equilibrium

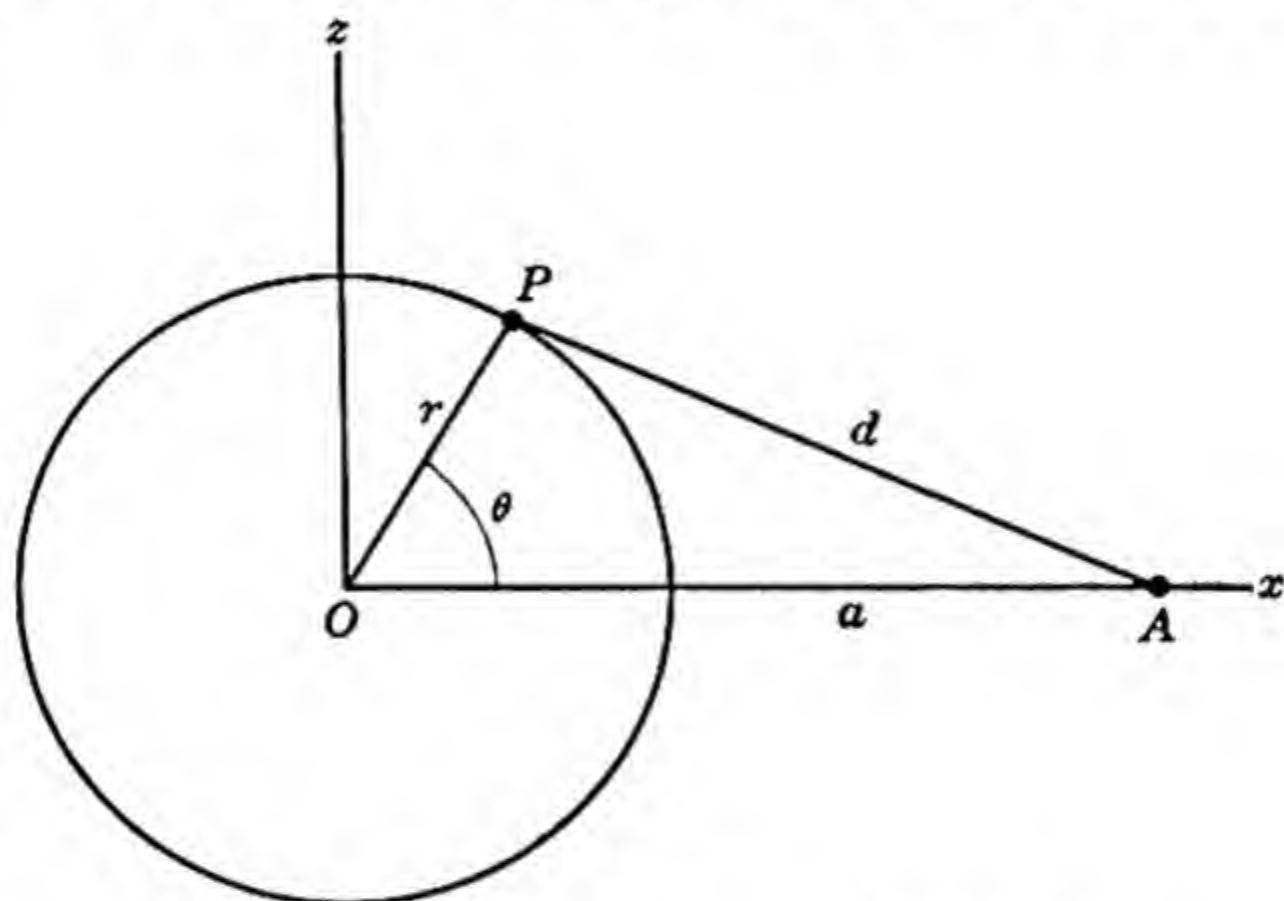


FIG. 50. Distances for molecule in cell

position at the center of its own cell. Since the interaction between molecules falls off rapidly with distance, it is sufficient to take into account only those molecules which are immediate neighbors to the given molecule. This is equivalent to a system consisting of a particle moving in the field of a number of other particles symmetrically arranged on the surface of a sphere. If the molecules surrounding a given molecule are closely packed, for example, in a manner analogous to a face-centered cubic lattice, the field within the cell produced by these molecules will be highly symmetrical. In these circumstances the actual field may be replaced by one which is spherically symmetrical about the center of the cell. The latter field may be regarded as equivalent to the average potential produced as the molecule within the cell describes a sphere about the center. It is probable that the conditions for the postulated model are most closely approximated by nonpolar molecules, especially those possessing spherical symmetry.

The adjective *cooperative* has been proposed for use in connection with systems in which the interaction potential between molecules depends on the total volume of the system. It is evident from what has been stated above that the cell model for the highly compressed gas makes the latter a cooperative system in this sense. It will be seen subsequently that the phenomenon

of condensation follows as a direct consequence of the same model; for this reason condensation has been referred as a *cooperative phenomenon*.

Let a be the average distance between molecules that are immediate neighbors; suppose one of these molecules is kept stationary at A , while the other is moved over the surface of a sphere of radius r , whose center O is at a distance of a from the molecule at A (Fig. 50). If P is taken as any position on the sphere, at a distance d from the point A , the mutual potential energy at P will then be represented by $u(d)$ where d is given by

$$d = (a^2 + r^2 - 2ar \cos \theta)^{1/2}. \quad (70.1)$$

In accordance with the arguments presented above, the average mutual potential $\bar{u}(r)$ of the two molecules is obtained by integrating $u(d)$ over the surface of the sphere and dividing by its area; thus,

$$\begin{aligned} \bar{u}(r) &= \frac{1}{4\pi r^2} \int_0^\pi \int_0^{2\pi} \{u(a^2 + r^2 - 2ar \cos \theta)^{1/2}\} r^2 \sin \theta d\theta d\phi \\ &= \frac{1}{2} \int_0^\pi \{u(a^2 + r^2 - 2ar \cos \theta)^{1/2}\} \sin \theta d\theta \\ &= \frac{1}{2} \int_0^\pi u(d) \sin \theta d\theta. \end{aligned} \quad (70.2)$$

If c is the number of nearest neighbors of a given molecule, the average potential energy $w(r)$ of the molecule within the cell, for which r is less than a , is

$$w(r) = c\bar{u}(r) = \frac{1}{2}c \int_0^\pi u(d) \sin \theta d\theta, \quad (70.3)$$

where d is defined by equation (70.1).

In order to proceed further with the calculations, it is necessary to postulate a function for the mutual potential energy of two molecules. A convenient choice, although not necessarily the only one, is to adopt the function of the form of equation (69.1) which was found to be satisfactory to account for the behavior of gases at low density. Further, in order to maintain, if possible, the continuity between these and the highly compressed gases now under consideration, the values of m and n will be taken as 6 and 12, respectively. The potential function to be employed in this work is, therefore,

$$u(r) = \frac{A}{r^{12}} - \frac{B}{r^6}, \quad (70.4)$$

so that equation (70.3) becomes

$$w(r) = \frac{1}{2}c \int_0^\pi \left(\frac{A}{d^{12}} - \frac{B}{d^6} \right) \sin \theta d\theta. \quad (70.5)$$

Upon introducing the value of d , according to equation (70.1), and carrying

out the integration, the result is

$$w(r) = \frac{1}{2}c \left[\frac{aA}{10ra^{12}} \left\{ \left(1 - \frac{r}{a}\right)^{-10} - \left(1 + \frac{r}{a}\right)^{10} \right\} - \frac{aB}{4ra^6} \left\{ \left(1 - \frac{r}{a}\right)^{-4} - \left(1 + \frac{r}{a}\right)^4 \right\} \right]. \quad (70.6)$$

In the limit when r approaches zero, equation (70.5) becomes

$$\begin{aligned} w(0) &= \frac{1}{2}c \int_0^r \left(\frac{A}{a^{12}} - \frac{B}{a^6} \right) \sin \theta d\theta \\ &= c \left(\frac{A}{a^{12}} - \frac{B}{a^6} \right), \end{aligned} \quad (70.7)$$

and making use of this result, it is possible to write equation (70.6) in the form

$$w(r) - w(0) = c \left\{ \frac{A}{a^{12}} l(y) - \frac{B}{a^6} m(y) \right\}, \quad (70.8)$$

where

$$y = \frac{r^2}{a^2}, \quad (70.9)$$

and the functions $l(y)$ and $m(y)$ are defined by

$$l(y) = (1 + 12y + 25.2y^2 + 12y^3 + y^4)(1 - y)^{-10} - 1 \quad (70.10)$$

and

$$m(y) = (1 + y)(1 - y)^{-4} - 1. \quad (70.11)$$

The volume v per single molecule is proportional to a^3 , and hence so also is the total volume V ; consequently, equation (70.8) may be written in the form

$$w(r) - w(0) = \Lambda \left\{ \left(\frac{V^*}{V} \right)^4 l(y) - 2 \left(\frac{V^*}{V} \right)^2 m(y) \right\}, \quad (70.12)$$

in which the constants Λ and V^* are chosen so that

$$\Lambda \left(\frac{V^*}{V} \right)^4 = \frac{cA}{a^{12}} \quad (70.13)$$

and

$$2\Lambda \left(\frac{V^*}{V} \right)^2 = \frac{cB}{a^6}. \quad (70.14)$$

It will be observed from the definitions (70.13) and (70.14) that

$$\Lambda = \frac{cB^2}{4A}, \quad (70.15)$$

and hence, by equation (69.11),

$$\Lambda = c|u_0|, \quad (70.16)$$

where $|u_0|$ is the potential energy at the minimum of the potential energy curve for the interaction between the two molecules (Fig. 47). Similarly, equation (70.7) may be written as

$$w(0) = \Lambda \left\{ \left(\frac{V^*}{V} \right)^4 - 2 \left(\frac{V^*}{V} \right)^2 \right\}. \quad (70.17)$$

Of the two equations (70.12 and (70.17)), the former represents the variation of the potential energy of a molecule as it moves in its cell, while the latter gives the potential energy at the center of the cell. It has been shown that the foregoing treatment is satisfactory only if the actual volume V is less than about $1.6V^*$; it will be seen shortly that at the critical point the volume is equal to $2V^*$, and so the arguments may be regarded as applicable at such high pressures that the volume of the gas is less than the critical volume.

70b. Partition Function for Highly Compressed Gas.—The partition function for the external degrees of freedom for a *single* molecule moving in a potential field within a cell can be represented by [cf. equation (67.23)],

$$Q_e = \frac{(2\pi mkT)^{3/2}}{h^3} \iiint e^{-u(r)/kT} dx dy dz.$$

Changing to spherical coordinates, and integrating over all values of the angles, this becomes

$$Q_e = \frac{(2\pi mkT)^{3/2}}{h^3} \int e^{-u(r)/kT} 4\pi r^2 dr, \quad (70.18)$$

or, omitting the translational factor, the configuration integral Q_u for the single molecule is given by

$$Q_u = 4\pi \int e^{-u(r)/kT} r^2 dr. \quad (70.19)$$

If the potential function is represented by equation (70.12), the energy zero being taken as that of the molecule in the center of the cell, i.e., when r is zero, then the configuration integral becomes

$$Q_u = 4\pi \int_0^{a/2} e^{-[w(r)-w(0)]/kT} r^2 dr. \quad (70.20)$$

The somewhat arbitrary choice of the upper limit of integration is justified by the argument that contributions to the partition function from portions of the cell outside the sphere of radius $\frac{1}{2}a$ must be small, owing to the re-

pulsive field, except perhaps at high temperatures. Upon changing the variable in equation (70.20) from r to y , by means of (70.9), the result is

$$Q_u = 2\pi a^3 \int_0^{1/4} y^{1/2} \exp \left[\frac{\Lambda}{kT} \left\{ 2 \left(\frac{V^*}{V} \right)^2 m(y) - \left(\frac{V^*}{V} \right)^4 l(y) \right\} \right] dy \quad (70.21)$$

$$= 2\pi a^3 g, \quad (70.22)$$

where g is used to represent the integral in equation (70.21).

The relation between the volume V and the quantity a^3 is given by the expression

$$a^3 = \gamma \frac{V}{N},$$

where γ is a constant dependent on the type of packing of the molecules surrounding the given molecule; for face-centered cubic packing, for example, γ is $\sqrt{2}$. Hence, it is possible to write equation (70.22) as

$$Q_u = 2\pi\gamma g \frac{V}{N} \quad (70.24)$$

As mentioned above, the energy zero is taken as that of a molecule at the center of its cell, but if the partition function (or configuration integral) is referred to the more usual energy zero represented by infinite separation of the molecules, it is necessary to multiply equation (70.24) by $e^{\epsilon_0/kT}$, where $-\epsilon_0$ is the average potential energy of a molecule at the center of its cell referred to the new zero value. Making this adjustment, the value of Q_u for the single molecule in its cell becomes

$$Q_u = 2\pi\gamma g \frac{V}{N} e^{\epsilon_0/kT}. \quad (70.25)$$

For N molecules, each of which is confined to its own cell, so that the gas may be treated virtually as a system of localized elements, the configuration integral Q_u would be Q_u^N . However, it is probable, in the gaseous state at least, that the molecules can move from cell to cell, so that the whole volume V , instead of V/N , is available to each of them. If this is the case, the molecules cannot be regarded as localized elements, and hence it is necessary to multiply Q_u by N , before raising to the N th power, to allow for the availability of the whole volume, and then to divide the result by $N!$ because the molecules are not localized. This matter will be discussed more fully later, especially in connection with the problem of the liquid state, but for the present it will be assumed that

$$Q_u = \frac{(Q_u N)^N}{N!}, \quad (70.26)$$

so that, introducing the Stirling approximation,

$$\ln Q_u = N \ln Q_u + N,$$

and by equation (70.24),

$$\ln Q_u = N \ln 2\pi\gamma g \frac{V}{N} + \frac{N\epsilon_0}{kT} + N. \quad (70.27)$$

As a first approximation, $-\epsilon_0$ will be equal to $\frac{1}{2}w(0)$, the factor $\frac{1}{2}$ being introduced so as to avoid counting twice the interaction between each pair of neighboring molecules. This value for $-\epsilon_0$ includes interactions of nearest neighbors only, and an improvement could be effected by introducing a term α to allow for interactions between molecules that are not nearest neighbors; thus,

$$-\epsilon_0 = \frac{1}{2}w(0) + \alpha.$$

It has been found that for a face-centered cubic structure, the effect of α is to increase the attractive term in the potential function by one-fifth, but the effect on the repulsive term is negligible; hence, using equation (70.17), it follows that

$$-\epsilon_0 = \Lambda \left\{ 0.5 \left(\frac{V^*}{V} \right)^4 - 1.2 \left(\frac{V^*}{V} \right)^2 \right\}. \quad (70.28)$$

Combining this result with equation (70.27), it is found that

$$\ln Q_u = N \left[\ln 2\pi\gamma g \frac{V}{N} + \frac{\Lambda}{kT} \left\{ 1.2 \left(\frac{V^*}{V} \right)^2 - 0.5 \left(\frac{V^*}{V} \right)^4 \right\} + 1 \right]. \quad (70.29)$$

The integral g is a function of Λ/kT and of V^*/V only [cf. equation (70.21)], and its value has been determined for various values of V^*/V ; hence, it may be supposed that $\ln Q_u$ can be calculated, provided Λ and V^* , which depend on A and B , by the definitions (70.13) and (70.14), are known. Examination of these equations shows that a and c must also be available; for face-centered packing a^3 is equal to $\sqrt{2}V/N$, as seen above, and under these conditions the number of nearest neighbors c is equal to 12.

The problem of setting up the partition function for a highly compressed gas, based on the postulated model, may thus be regarded as solved; the complete partition function Q , for the system of N molecules, equal to $Q_e Q_u$, is given by

$$Q = \left\{ \frac{(2\pi mkT)^{3/2}}{h^3} \right\}^N Q_u Q_e. \quad (70.30)$$

70c. Equation of State: The Critical State.—For the present it is desired to derive an equation of state, and hence use may be made of the relationship

$$P = kT \left(\frac{\partial \ln Q_u}{\partial V} \right)_T,$$

which gives, from equation (70.29),

$$P = \frac{NkT}{V} \left[1 - \frac{\Lambda}{kT} \left\{ 2.4 \left(\frac{V^*}{V} \right)^2 - 2 \left(\frac{V^*}{V} \right)^4 \right\} - \frac{4\Lambda}{kT} \left\{ \left(\frac{V^*}{V} \right)^2 \frac{g_m}{g} - \left(\frac{V^*}{V} \right)^4 \frac{g_l}{g} \right\} \right] \quad (70.31)$$

where g_l and g_m , like g , are functions of Λ/kT and V^*/V only; they are defined by

$$g_l = \int_0^{1/4} y^{1/2} l(y) \exp \left\{ -\frac{\Lambda}{kT} \left(\frac{V^*}{V} \right)^4 l(y) + 2 \frac{\Lambda}{kT} \left(\frac{V^*}{V} \right)^2 m(y) \right\} dy \quad (70.32)$$

and

$$g_m = \int_0^{1/4} y^{1/2} m(y) \exp \left\{ -\frac{\Lambda}{kT} \left(\frac{V^*}{V} \right)^4 l(y) + 2 \frac{\Lambda}{kT} \left(\frac{V^*}{V} \right)^2 m(y) \right\} dy. \quad (70.33)$$

Attention should be called to the fact that the equation of state (70.31) is independent of any assumption concerning the localized or nonlocalized nature of the molecule in its cell; this is because the partition functions for

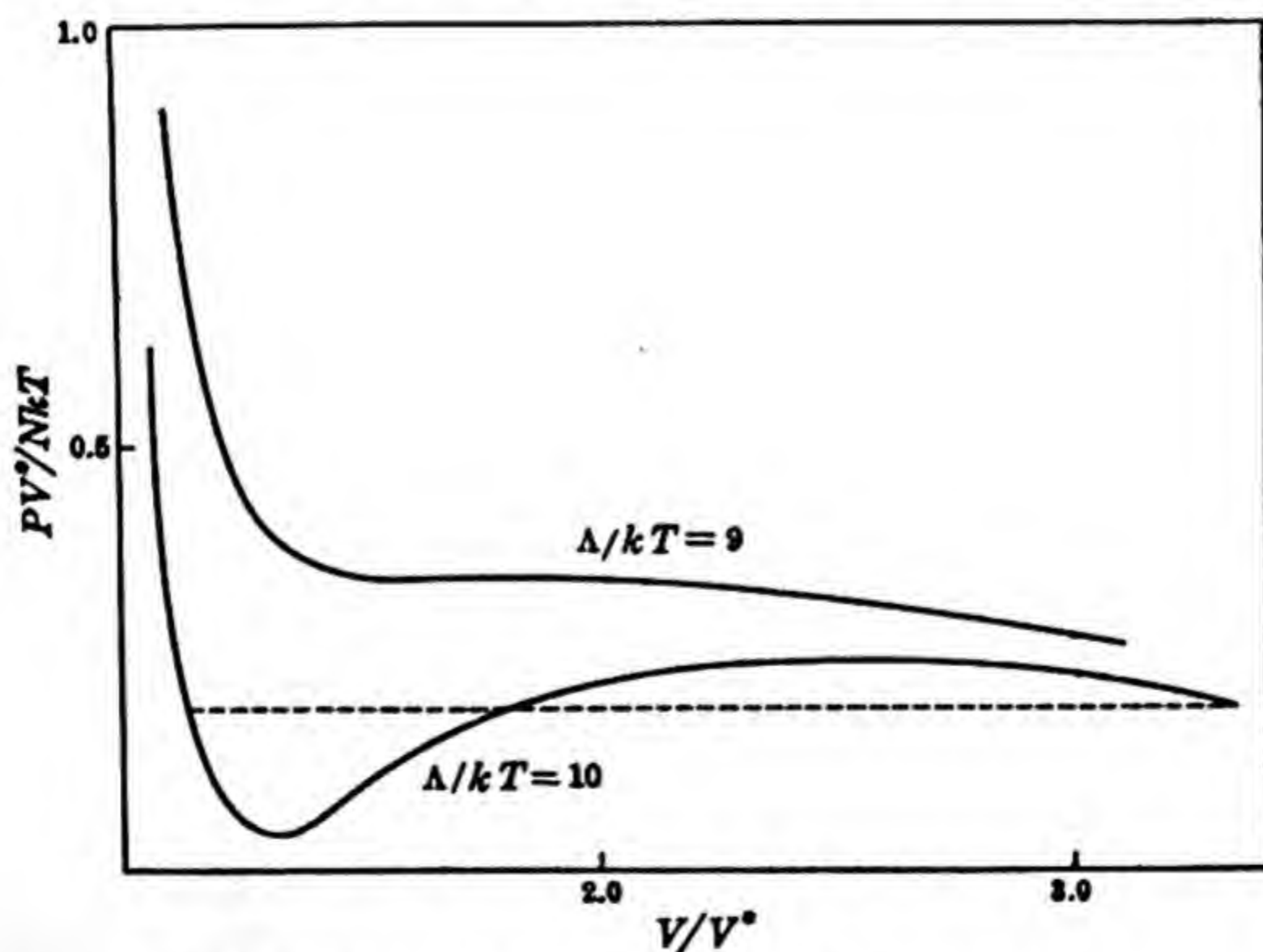


FIG. 51. Plot of equation of state for imperfect gas

the two cases differ only by a constant factor, which in any event gives zero upon differentiation. For other thermodynamic properties, however, such as entropy and free energy, which involve $\ln Q$, the results are affected by the particular choice that is made (cf. Section 56e).

The values of g , g_l and g_m , obtained by numerical integration, have been determined and tabulated for two values of Λ/kT , viz., 9 and 10, and for a range of V/V^* values; from these functions, the form of the isotherms, as represented by the plot of PV^*/NkT against V/V^* , were calculated by means of equation (70.31). The results obtained in this manner are depicted in Fig. 51; it is apparent that the curve for $\Lambda/kT = 10$ corresponds to the case in which liquefaction occurs as the pressure is increased, whereas the curve for $\Lambda/kT = 9$ appears to represent almost exactly the conditions for the critical isotherm. It follows, therefore, that the perfectly general rule

$$\frac{\Lambda}{kT_c} = 9$$

or

$$T_c = \frac{\Lambda}{9k} \quad (70.34)$$

may be derived on the basis of the postulated model. Further, utilizing equation (70.15), with c equal to 12, for face-centered cubic packing, it is seen that equation (70.34) may be written as

$$T_c = \frac{4|u_0|}{3k}. \quad (70.35)$$

It is thus possible, by means of the $|u_0|/k$ data in Table XXV, to calculate the critical temperatures of the various gases; these results are compared with the experimental values in Table XXVI. The data for helium are not

TABLE XXVI. CRITICAL TEMPERATURES OF GASES

Gas	$\frac{ u_0 }{k}$	T_c Calc.	T_c Obs.
Ne	35.7	47.6° K	44° K
Ar	120.0	160.0	150
H ₂	31.0	41.3	33
N ₂	96.7	128.9	126

included since the critical temperature of this gas is 5.2° K, and in this vicinity there is likely to be considerable gas degeneration; nevertheless, it is significant to record that the value of T_c calculated from equation (70.35) is 8.0° K. The agreement between calculated and observed results in Table XXVI is seen to be satisfactory. It is of interest to mention, however, that there is some experimental evidence that the average value of c , the number of nearest neighbors to a given molecule in a normal liquid is 11, instead of 12. If this change were made, T_c would be equal to $11|u_0|/9k$, and the agreement for neon, argon and hydrogen would be even better than that recorded above.

According to the results in Table XXV, the value of $kT_B/|u_0|$, where T_B is the Boyle point, is equal to 3.43, in the case in which the indices m and n in the bireciprocal potential function are 6 and 12, respectively. According

to equation (70.35), $kT_c/|u_0|$ for the same potential function is equal to $\frac{3}{4}$; hence

$$\frac{T_B}{T_c} = 3.43 \times \frac{3}{4} = 2.57.$$

The experimental ratio of these two temperatures for a number of substances lies in the range of 2.5 to 2.7. As might be expected, hydrogen and helium are exceptional in this respect, as these gases probably show gas degeneration, because of the failure of classical statistics, at the low temperatures involved. It may be mentioned, incidentally, that the van der Waals equation leads to a value of 3.375 for the ratio of T_B to T_c .

The critical volume should be determinable from the position of the point of inflection in the critical isothermal in Fig. 51; it is evident from the shape of the curve that this point cannot be estimated with any degree of accuracy, but it occurs when V/V^* is approximately equal to 2; hence, the molar critical volume is given by

$$V_c \approx 2V^*. \quad (70.36)$$

Combination of equations (69.4), (70.13) and (70.14) gives the result

$$\frac{V^*}{V} = \frac{r_0^3}{a^3},$$

and hence from equation (70.23),

$$V^* = \frac{Nr_0^3}{\gamma}, \quad (70.37)$$

so that (70.36) becomes

$$V_c \approx \frac{2Nr_0^3}{\gamma}$$

where N is the Avogadro number. If γ is taken as $\sqrt{2}$, for face-centered cubic packing, the molar critical volume can be calculated from the r_0 values given in Table XXV.

70d. Equilibrium Between Liquid and Vapor.—The cell model of a highly compressed gas treated in the preceding sections has been shown to be satisfactory in the vicinity of the critical point, and hence it should be equally, or more, valid at greater densities. It is therefore to be regarded as applicable to liquids although, of course, not to the vapors with which they are in equilibrium, since the density of the latter will not, in general, be sufficiently high. It is nevertheless possible to study liquid-vapor equilibria by utilizing the partition function for the liquid based on the cell model, whereas the vapor is usually at a low enough pressure to be treated as an ideal gas. At equilibrium, the molar free energies of the two phases will be equal, and this fact can be utilized to derive an expression for the vapor pressure of a liquid as a function of temperature.

The molar free energy of the liquid is given by [cf. equations (67.5) and (67.8)]

$$F_l = -kT \ln Q + PV_l,$$

and from equation (70.30), together with the expression for $\ln Q$ [equation (70.27)], it follows that

$$F_l = -NkT \ln \frac{(2\pi mkT)^{3/2}}{h^3} - NkT \ln 2\pi\gamma g \frac{V_l}{N} - NkT - N\epsilon_0 - NkT \ln Q_i, \quad (70.38)$$

the term PV_l having been neglected for the liquid since it is small in comparison with NkT . It should be noted that the molar volume V_l of the liquid has been used for V in the second term on the right-hand side; further Q_i has been replaced by Q_i^N .

The free energy of a mole of vapor, assumed to behave as a perfect gas, can be represented in terms of the partition function per molecule by means of equation (56.9), viz.,

$$\begin{aligned} F_g &= -NkT \ln \frac{Q}{N} \\ &= -NkT \ln \frac{(2\pi mkT)^{3/2}}{h^3} \cdot \frac{kT}{p} - NkT \ln Q_i, \end{aligned} \quad (70.39)$$

where the translational contribution to the partition function has been written in the form of equation (57.6), so as to introduce the pressure p of the vapor. When liquid and vapor are in equilibrium, F_l and F_g will be equal; the pressure p will then be the equilibrium vapor pressure at the temperature T . Comparing equations (70.38) and (70.39), and assuming that the internal partition function Q_i is the same for both liquid and vapor, it follows that

$$\begin{aligned} \ln p &= -\ln 2\pi\gamma g \frac{V_l}{NkT} - \frac{\epsilon_0}{kT} - 1, \\ \therefore p &= \frac{NkT}{2\pi\gamma g V_l} e^{-(\epsilon_0 + kT)/kT}. \end{aligned} \quad (70.40)$$

The vapor pressure equation (70.40) may be rewritten in the form

$$p = \frac{N\Lambda}{V^*} \Omega \quad (70.41)$$

where Ω , defined by,

$$\ln \Omega = \ln \frac{V^*}{2\pi\gamma g V_l} + \ln \frac{kT}{\Lambda} - \frac{\epsilon_0 + kT}{kT}, \quad (70.42)$$

is a function of Λ/kT and V^*/V_l only; this will be evident from the fact that the integral g , as given by equation (70.21), and ϵ_0 , defined by equation (70.28), are both functions of these two variables only.

Since PV_l for a liquid is usually negligibly small in comparison with NkT , the whole expression in the square brackets in equation (70.31) may be taken as approximately equal to zero; hence, it is possible to write with fair accuracy

$$\frac{\Lambda}{kT} \left\{ 2.4 \left(\frac{V^*}{V_l} \right)^2 - 2 \left(\frac{V^*}{V_l} \right)^4 \right\} - \frac{4\Lambda}{kT} \left\{ \left(\frac{V^*}{V_l} \right)^2 \frac{g_m}{g} - \left(\frac{V^*}{V_l} \right)^4 \frac{g_l}{g} \right\} = 1. \quad (70.43)$$

It has been seen previously that g , g_l and g_m , are functions of Λ/kT and V^*/V_l only; hence, this equation provides a direct connection between Λ/kT and V^*/V_l . Since these two quantities are related, it follows that Ω , defined by equation (70.42), may be regarded as a function of Λ/kT only. As a result of calculating the values of Ω for various values of Λ/kT , it has been found, at least within the range of Λ/kT from 12.8 to 21, that $\ln \Omega$ is given with good accuracy by the expression

$$\ln \Omega = 1.916 - 0.678 \frac{\Lambda}{kT},$$

and hence from equation (70.41),

$$\ln p = \ln \frac{N\Lambda}{V^*} + 1.916 - 0.678 \frac{\Lambda}{kT}. \quad (70.44)$$

Since Λ and V^* are known in terms of $|u_0|$ and r_0 , respectively, by equations (70.16) and (70.37), it should be possible to derive from these two latter quantities the vapor pressure of a liquid.

It will be noted that equation (70.44) is of the correct form for representing the variation of vapor pressure with temperature, but a more stringent test may be applied by using it to calculate boiling points, that is, to calculate the temperature (T_b) at which the vapor pressures of various liquids become equal to one atmosphere. The results for neon, nitrogen and argon are quoted in Table XXVII; the agreement between calculated and experimental

TABLE XXVII. CALCULATION OF BOILING POINTS

Gas	$\Lambda \times 10^{16}$ (ergs/molecule)	V^*/N (\AA^3)	Boiling Point		T_b/T_c	
			Calc.	Obs.	Calc.	Obs.
Ne	58.7	20.6	29.6° K	27.2° K	0.62	0.61
N ₂	159	51.3	79.0	77.2	0.61	0.61
A	199	38.9	94.3	87.4	0.59	0.58

boiling points is good. The calculations based on classical statistics cannot evidently be applied to hydrogen and helium, but it may be noted that the calculated boiling point of the former is 26.4° K, compared with the observed value of 20.3° K.

A further test of the liquid model under consideration may be obtained by evaluating the ratio of the calculated boiling point T_b to the calculated critical temperature T_c as given in Table XXVI; the coincidence between the theoretical and observed ratios is excellent. It will be noted that the ratio T_b/T_c is constant for various liquids, both theoretically and experimentally; since Λ/kT has a definite value, namely 9, at the critical temperature, it follows that this quantity, i.e., Λ/kT_b , should be constant for all substances at their boiling points. The results, indicate, in fact, that Λ/kT_b is approximately equal to 16, for atmospheric pressure. Further, since kT_c is equal to $\frac{4}{3}|\mu_0|$, as given by equation (70.35), it follows that

$$kT_b \approx 0.8|\mu_0|. \quad (70.45)$$

This relationship provides a simple method for calculation of the boiling point.

70e. Heat and Entropy of Vaporization.—Utilizing the thermodynamic relationship,

$$\left(\frac{\partial \ln p}{\partial T}\right)_P = \frac{\Delta H_e}{NkT^2}, \quad (70.46)$$

in which ΔH_e is the molar heat of evaporation, in conjunction with equation (70.44), it is seen that

$$\Delta H_e = 0.678N\Lambda, \quad (70.47)$$

and so the heat of vaporization of a liquid at the normal boiling point can be derived from the known value of Λ or of $|\mu_0|$. If ΔH_e is divided by the boiling point, the result is the entropy of vaporization, and an approximate calculation of the latter may be made by utilizing the fact mentioned above that Λ/kT_b is approximately 16, where T_b is the boiling point at atmospheric pressure. It follows, then, that

$$\begin{aligned} \frac{\Delta H_e}{T_b} &= 0.678 \times 16Nk \\ &= 21 \text{ cal.,} \end{aligned}$$

should be constant in accordance with Trouton's law.

An examination of equation (70.44) shows that the entropy of vaporization will be strictly constant only if $\ln \Lambda/V^*$ is constant for all liquids. This is the condition for Trouton's law to be exactly applicable. According to the modified law due to Hildebrand, the entropy of vaporization is constant under such conditions that the molar concentration of the saturated vapors are the same. This rule is in better agreement with observation than is that of Trouton, and the reason is apparent from the following considerations. If n_g is the number of molecules per unit volume of the vapor, then

$$p = kTn_g,$$

assuming the vapor to behave ideally; combination of this result with

equation (70.44) then gives

$$\ln n_0 = \ln \frac{N}{V^*} + \ln \frac{\Lambda}{kT} + 1.916 - 0.678 \frac{\Lambda}{kT}.$$

It follows from this equation that if the entropy of vaporization, which is equal to $0.678N\Lambda/T_b$, is to remain constant at constant n_0 , the value of $\ln V^*$ must be constant. It appears, in general, that V^* for different substances is more likely to be constant than is Λ/V^* , and hence the Hildebrand rule will be superior to that of Trouton.

It may be remarked, in conclusion, that the results of this section, as well as those of preceding sections, are probably more strictly applicable to nonpolar molecules. This is undoubtedly one reason why the rules of Trouton and Hildebrand do not hold for polar and associated substances. For such compounds the potential fields are not symmetrical, and the model postulated at the beginning of Section 70a cannot be regarded as satisfactory.

70f. The Free Volume of a Liquid.⁹—In the foregoing approximate treatment of the liquid state, the thermodynamic properties of the liquid have been developed from those of the highly compressed gas. Another approach, based on essentially the same model, has been used in which some of the properties of the liquid are employed to derive others. It was seen in Section 67d that for a perfect gas, when the interaction potential is zero, the configuration integral, as defined by equation (67.24), becomes equal to V^N , where N is the number of molecules and V is the total volume of the system. It would seem reasonable, therefore, to represent the configuration integral in the alternative form

$$Q_u = V_f^N e^{-E/RT}, \quad (70.48)$$

where the significance of V_f , which is called the *free volume*, will be considered shortly. The potential function $U(q)$ in equation (67.24) is, of course, by definition, a function of the coordinates, and hence of the configuration of the molecules; in equation (70.48) this has been replaced by a mean value E per mole, averaged over all accessible configurations. Actually E may be identified with the hypothetical energy of vaporization, i.e., the difference in energy between the liquid and the gas, in which there is no interaction, at the absolute zero. According to equation (70.48), therefore, V_f/N , the free volume per molecule, may be regarded as the effective volume accessible to the center of a molecule in a liquid. In this volume the potential is assumed to have a uniform value E , with a sharp rise to infinity at the boundary; the actual increase of potential is not so sudden as this would imply, but since repulsive forces decrease rapidly with distance, the approximation is not too serious. The concept of free volume is an extension of

⁹ Lennard-Jones and Devonshire, ref. 8; Eyring and Hirschfelder, *J. Phys. Chem.*, **41**, 249 (1937); Kincaid and Eyring, *J. Chem. Phys.*, **6**, 620 (1938); Hirschfelder, *J. Chem. Ed.*, **16**, 540 (1939); Kincaid, Eyring and Stearn, *Chem. Rev.*, **28**, 301 (1941); Fowler and Guggenheim, ref. 1, p. 331.

the idea that each molecule is enclosed by its neighbors in a cell; the free volume is, however, not the whole cell volume, but rather the average volume in which the *center* of the molecule can move inside the hypothetical cell due to the repulsion of surrounding molecules.

If each molecule were confined within the cell, and were unable to escape, the complete partition function would be

$$Q_s = \left\{ \frac{(2\pi mkT)^{3/2}}{h^3} \cdot \frac{V_f}{N} \right\}^N (Q_i e^{-E/RT})^N, \quad (70.49)$$

since each of the N molecules behaves like an ideal gas molecule moving within its own volume V_f/N . However, if, as indicated in Section 70b, the molecules are not to be regarded as localized elements, each completely confined to its own cell, it is necessary to introduce the factor $1/N!$. Thus, if the whole of the free volume V_f is available to all the N molecules, the complete partition function for the system would be

$$Q_l = \frac{1}{N!} \left\{ \frac{(2\pi mkT)^{3/2}}{h^3} V_f \right\}^N (Q_i e^{-E/RT})^N. \quad (70.50)$$

In order to distinguish between the two partition functions represented by equations (70.49) and (70.50), the former is indicated by the subscript s to indicate that the partition function would represent that for the solid state, in which the molecules are localized (cf. Section 67c), while the latter has the subscript l to show that it refers to the liquid state.

By utilizing equation (67.9) for the entropy of a system of N molecules, it is seen from equations (70.49) and (70.50) that the change of entropy ΔS_f in melting (fusion), which is equal to $S_l - S_s$, is given by

$$\begin{aligned} \Delta S_f &= S_l - S_s \\ &= k \ln \frac{N^N}{N!}, \end{aligned} \quad (70.51)$$

the assumption being made that V_f will be the same in solid and liquid, and that the contribution Q_i of the internal degrees of freedom to the partition function is unchanged on melting. Introducing the Stirling approximation, it follows from equation (70.51) that

$$\Delta S_f = kN = R \text{ per mole per degree.} \quad (70.52)$$

This increase of entropy accompanying melting is due merely to the postulates that the whole of the free volume is available to each molecule in the liquid state, whereas in the solid the molecule is restricted to its own cell. For this reason the entropy change of R per mole arrived at in this manner has been called the *communal entropy*.¹⁰ This will not represent the whole

¹⁰ Eyring and Hirschfelder, ref. 9; Hirschfelder, Stevenson and Eyring, *J. Chem. Phys.*, 5, 896 (1937).

of the entropy of fusion, but it should, according to the foregoing arguments, constitute the major portion, the remainder being due to the volume change accompanying fusion.

It is an undoubted fact that for many metals, for which the contributions of internal degrees of freedom are usually the same in the liquid and solid states, the entropies of fusion are in the range of 1.7 to 2.3 cal./mole/degree (E.U.), in accordance with the requirements of the foregoing treatment. Further, where there is evidence of restricted rotation in the solid state changing over to free rotation in the liquid, the entropy of fusion, as is to be expected, is in excess of 2 E.U. In spite of this general agreement, the view is now usually accepted that the change from solid to liquid does not involve a sudden transition from complete restriction to complete freedom of movement of the molecules, accompanied by the introduction of the whole of the communal entropy.¹¹ The expressions given above, viz., equations (70.49) and (70.50), for the partition functions of solid and liquid are thus not exact at the melting point, although they may be reasonably satisfactory at lower and higher temperatures, respectively. Various modifications of the treatment will be given later, but for the present the partition functions derived above will be employed.

70g. Determination of Free Volumes.—Several methods have been proposed for the calculation of the free volume of a liquid. If the potential field is of the type postulated above, namely uniform within the cell but rising very sharply at the boundaries, it is possible to make an estimate of the free volume in the following manner. Suppose, for simplicity, that there is cubic packing of the molecules in the liquid; one molecule may be considered as oscillating about the origin, and the six nearest neighbors are regarded as being fixed in their mean positions along three axes. One of these axes is shown in Fig. 52; if v is the mean volume per molecule in the liquid, then each molecule is at a distance $v^{1/3}$ from the origin. If d is the incompressible diameter of a molecule, $2v^{1/3} - 2d$ is the distance the central atom is free to move along each axis, and the free volume per single molecule is then given by

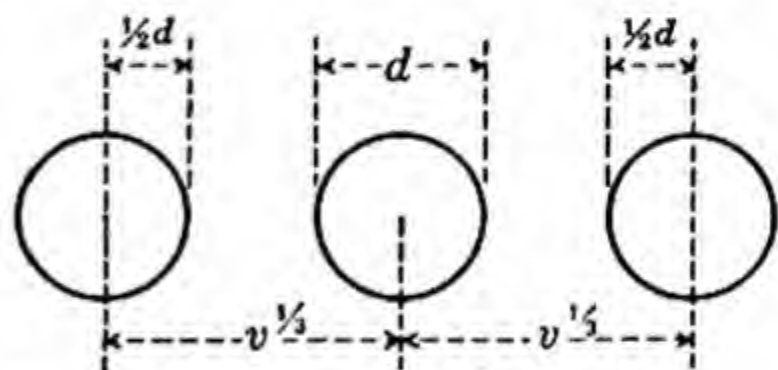


FIG. 52. Calculation of free volume

$$v_f = (2v^{1/3} - 2d)^3 = 8(v^{1/3} - d)^3. \quad (70.53)$$

It is probable that a similar equation will hold for other types of molecular packing, so that, in general,

$$v_f = b^3(v^{1/3} - d)^3$$

or

$$V_f = Nb^3(v^{1/3} - d)^3, \quad (70.54)$$

where b depends on the packing and may vary with temperature.

¹¹ Rice, *J. Chem. Phys.*, 6, 476 (1938); see also, ref. 18.

In order to make use of this expression, it is necessary to consider the subject from another angle. The general equation relating the pressure of a liquid to the partition function is

$$P = kT \left(\frac{\partial \ln Q_l}{\partial V} \right)_T,$$

and hence from equation (70.50)

$$P = NkT \left(\frac{\partial \ln V_f}{\partial V} \right)_T - \left(\frac{\partial E}{\partial V} \right)_T,$$

$$\therefore P + \left(\frac{\partial E}{\partial V} \right)_T = NkT \left(\frac{\partial \ln V_f}{\partial V} \right)_T. \quad (70.55)$$

From equation (70.54),

$$\frac{\partial \ln V_f}{\partial V} = \frac{1}{V_f} \cdot \frac{\partial V_f}{\partial V} = bV_f^{-1/3}V^{-2/3}, \quad (70.56)$$

where V is the molar volume of the liquid; if this result is introduced into equation (70.55), then

$$\left\{ P + \left(\frac{\partial E}{\partial V} \right)_T \right\} V_f^{1/3} V^{2/3} = bRT, \quad (70.57)$$

and upon solving for V_f , it is found that

$$V_f = \left\{ \frac{bRT}{P + \left(\frac{\partial E}{\partial V} \right)_T} \right\}^3 \frac{1}{V^2}. \quad (70.58)$$

The variation of the mean potential energy E with volume is not known, but it appears from certain experimental data that it may be replaced without serious error by the quantity $\Delta E_v/V$, where ΔE_v is the energy of vaporization per mole of liquid at the specified temperature. Further, the pressure P may be neglected in comparison with $\partial E/\partial V$, so that

$$V_f = \left(\frac{bRT}{\Delta E_v} \right)^3 V, \quad (70.59)$$

where, for many liquids, b is equal to 2.

Another method of deriving the free volume makes use of the velocity of sound in the liquid. For most liquids the velocity of sound is 5 to 10 times as great as the average kinetic-theory velocity of the molecules; this difference can arise in the following manner. Suppose there are three molecules A , B and C (Fig. 53), in a line, and suppose the wave front travels from the inner edge of the molecule A to the adjacent edge of B by the velocity

of sound (u_0) applicable to an ideal gas; this is given by kinetic theory as

$$u_0 = \left(\frac{RT\gamma}{M} \right)^{1/2}, \quad (70.60)$$

where γ is here the ratio of the specific heats of the gas and M is its molecular weight. As A collides with B , however, the signal is transmitted almost instantaneously to the opposite edge of B ; thus, although the wave front moves apparently through the distance $v_f^{1/3}$, it effectively travels a distance $v^{1/3}$, as seen in Fig. 53, and consequently

$$\frac{u_l}{u_0} = \left(\frac{v}{v_f} \right)^{1/3}, \quad (70.61)$$

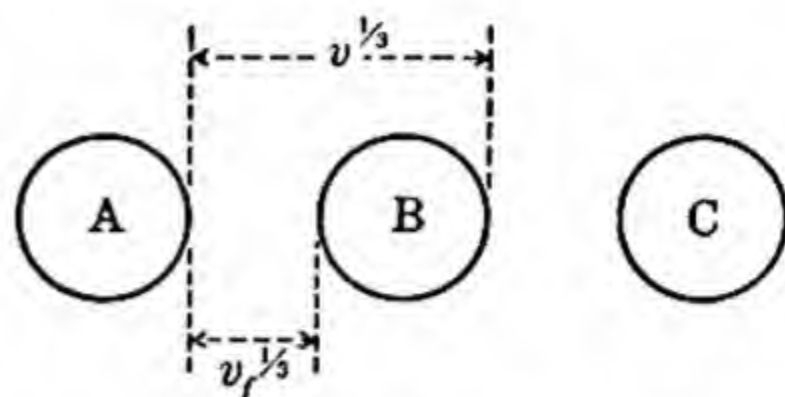


FIG. 53. Free volume from velocity of sound

where u_l is the velocity of sound in the liquid. It follows, therefore, from equations (70.60) and (70.61), that V_f , the free volume per mole, is given by

$$V_f = \frac{V}{u_l^3} \left(\frac{RT\gamma}{M} \right)^{3/2}, \quad (70.62)$$

and so the value can be determined from the known velocity of sound in the liquid. The results for the free volumes of a number of liquids at 20° C calculated by the two methods described here are given in Table XXVIII;

TABLE XXVIII. FREE VOLUMES OF LIQUIDS

Liquid	Free Volume	
	From Energy of Vaporization	From Velocity of Sound
Acetone	0.54 cc.	0.45 cc.
Ether	0.65	0.70
Chloroform	0.34	0.29
Toluene	0.22	0.22
Carbon tetrachloride	0.31	0.28
Carbon disulfide	0.58	0.30

the agreement between the two sets of results is very fair, on the whole, but the velocity of sound method is probably more to be relied upon in cases of doubt.

70h. Liquid Mercury and Monatomic Metals.¹²—When applied to liquid mercury, the two methods for calculating the free volume give results that are appreciably different. The type of potential used in the first treatment is shown in Fig. 54 *A*, but it is probable that the form in Fig. 54 *B* is more satisfactory, especially at higher temperatures. This curve may be regarded as a combination of the potential of type *A* with the parabolic type of potential characteristic of a harmonic oscillator. The contribution to the

¹² Kincaid and Eyring, *J. Chem. Phys.*, 5, 587 (1937).

free volume of the former potential energy will be similar to that already considered, and hence will be given by equation (70.54); for the present purpose the linear dimensions of the free volume may be written as

$$(V_f')^{1/3} = N^{1/3}b \left\{ \left(\frac{V}{N} \right)^{1/3} - \left(\frac{V_0}{N} \right)^{1/3} \right\}, \quad (70.63)$$

where V_0/N is equal to d^3 , and V_0 would represent the total volume occupied by the N molecules when closely packed, as in the solid state. The second contribution $(V_f'')^{1/3}$ may be regarded as due to the harmonic oscillations of the atom; thus

$$(V_f'')^{1/3} = N^{1/3} \int_{-\infty}^{\infty} e^{-f x^2 / 2kT} dx, \quad (70.64)$$

in which f is the force constant, defined in the usual manner, in terms of the vibration frequency ν and the mass m of the particle, by

$$\nu = \frac{1}{2\pi} \sqrt{\frac{f}{m}}. \quad (70.65)$$

Carrying out the integration of equation (70.64), and introducing equation (70.65),

$$(V_f'')^{1/3} = \frac{N^{1/3}}{\nu} \left(\frac{kT}{2\pi m} \right)^{1/2}. \quad (70.66)$$

The frequency ν may be determined from the Einstein characteristic temperature θ_E , which may be taken as equal to $h\nu/k$.¹³ It is thus possible to evaluate both $(V_f')^{1/3}$ and $(V_f'')^{1/3}$ and the cube of the sum of these should give the total free volume. The value calculated for mercury agrees with that derived from the velocity of sound over a large range of temperatures and pressures. The modified method of determining free volumes should probably be used for all monatomic metals, and possibly also for the inert gases in the liquid state.

70i. Applications of the Free Volume Concept.¹⁴—A simple equation for vapor pressure in terms of the free volume can be derived in the familiar manner, by equating the free energies of liquid and vapor states. Assuming

¹³ The Einstein characteristic temperature θ_E , which is related to the average frequency ν , is equal to $\frac{3}{2}\theta$, where θ is the Debye characteristic temperature defined in Section 54b.

¹⁴ See refs. 9 and 12.

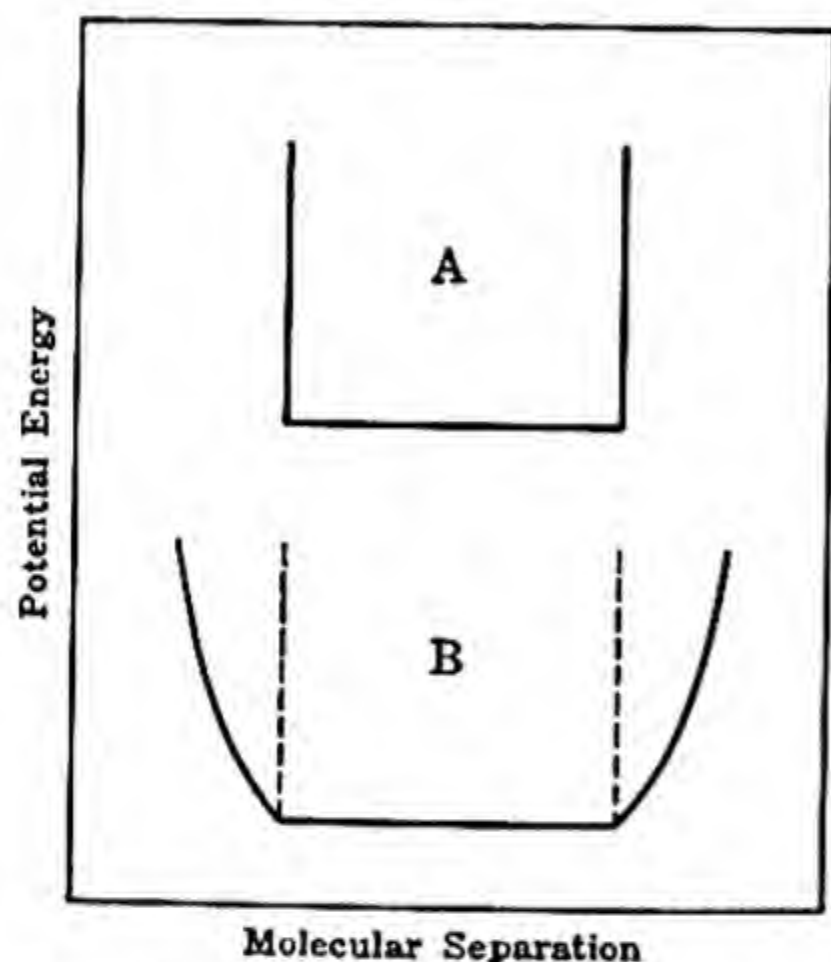


FIG. 54. Potential energy curves for monatomic liquid metal

the latter to behave ideally, then [cf. equation (70.39)],

$$F_g = -NkT \ln \frac{(2\pi mkT)^{3/2}}{h^3} \cdot \frac{kT}{p} - NkT \ln Q_i, \quad (70.67)$$

where p is the pressure of the vapor; further, since

$$F_l = -kT \ln Q_l + PV_l,$$

it follows from equation (70.50) that

$$F_l = -NkT \ln \frac{(2\pi mkT)^{3/2}}{h^3} \cdot \frac{V_l}{N} - NkT \ln Q_i + E - NkT + PV_l. \quad (70.68)$$

If Q_i is assumed to be the same in both liquid and vapor, it is apparent that

$$p = \frac{RT}{V_l} e^{-\Delta H_e/RT}, \quad (70.69)$$

in which ΔH_e is the heat of vaporization, defined by

$$\Delta H_e = -E + RT - PV_l. \quad (70.70)$$

It is thus seen that equation (70.69) provides a simple relationship between the vapor pressure and the free volume. If equation (70.59) for the free volume is now introduced, it follows that

$$p = \frac{(\Delta E_e)^3}{b^3 R^2 T^2 V_l} e^{-\Delta H_e/RT}, \quad (70.71)$$

V_l being used in place of V to indicate the molar volume of the liquid. If the vapor behaves ideally, it is possible to write

$$\Delta H_e = \Delta E_e + RT,$$

and hence equation (70.71) becomes

$$p = \frac{RT}{b^3 V_l} \left(\frac{\Delta H_e}{RT} - 1 \right)^3 e^{-\Delta H_e/RT}, \quad (70.72)$$

or, taking b as equal to 2, for a simple cubic lattice,

$$p = \frac{RT}{8V_l} \left(\frac{\Delta H_e}{RT} - 1 \right)^3 e^{-\Delta H_e/RT}. \quad (70.73)$$

The vapor pressure of the liquid can thus be calculated from the heat of vaporization and the molar volume.

From this equation it is possible to derive both the Hildebrand and Trouton rules. For example, if the vapor concentrations are the same for a number of substances, then p/RT will be constant; it follows then from

equation (70.73) that $\Delta H_e/T$ will be a function of V only. If the molar volumes of the various substances are approximately the same in the liquid state, then $\Delta H_e/T$ should be constant, in accordance with Hildebrand's rule. In any event, since $\Delta H_e/T$ appears in the exponential term, the value of this quantity, as given by equation (70.73), does not depend greatly on the molar volume.

If the vapor pressures are fixed at 1 atm., the corresponding temperatures are then the boiling points of the various substances. For the more common liquids, the boiling points may be supposed to lie within the range of 300° to 450° K, while the molar volumes vary from 80 to 120 cc.; substituting these values in equation (70.73), and introducing the appropriate value of R in atm. cc./degree, it is found that

$$\frac{\Delta H_e}{T_b} \approx 10R,$$

which is approximately 20 cal. per mole per degree, in agreement with Trouton's law. Although this result has been derived for a particular range of boiling points and molar volumes, it is actually not very sensitive to variations in these properties.

Both the temperature coefficient of thermal expansion (α) and the compressibility (β) of the liquid may be calculated, provided the average potential energy E can be expressed as a function of the volume. For this purpose equations (70.54) and (70.57) are combined so as to eliminate the packing factor b ; the result is

$$\left(P + \frac{\partial E}{\partial V} \right) (V - V^{2/3}N^{1/3}d) = RT,$$

and since P is small in comparison with $\partial E/\partial V$, it follows that

$$\frac{\partial E}{\partial V} (V - V^{2/3}N^{1/3}d) = RT. \quad (70.74)$$

Making the assumption that E may be written as a function aV^{-n} of the volume, where a and n are constants, it is seen that

$$\frac{\partial E}{\partial V} = -\frac{nE}{V}.$$

With this result, it is possible by differentiating equation (70.74) with respect to the temperature to obtain α , while differentiation with respect to the pressure gives β .

STATISTICAL MECHANICS OF CRITICAL STATE

71a. Complete Treatment of Imperfect Gases.—In the evaluation of the configuration integral in Section 67d, all terms in equation (67.32) beyond the second were neglected; as already pointed out, this means that binary

encounters only were considered in the evaluation of the potential energy of the system of molecules. The results obtained in this manner are approximate, and can be regarded as applicable only under such conditions, e.g., low density, that binary encounters between molecules predominate very greatly over all other types. For the complete statistical treatment of gases at high pressures, and especially when condensation phenomena are being considered, it is necessary to take into account the mutual interactions between three, four, etc., as well as between two, molecules. The problem presents enormous difficulties, and hence the alternative, approximate but simple, approach described in Section 70 was developed. However, an important advance in the statistical mechanical treatment of highly compressed gases has been made by Mayer;¹⁵ owing to the complexity of the subject it is proposed to give here a general outline only of the method of treatment and of the results obtained.

The approach to the problem is based entirely on statistical mechanics, and involves the introduction of the concept of *clusters*. A cluster is defined as a group of molecules in which each member is sufficiently close to at least one other member of the group as to make the mutual potential energy significantly different from zero. The number of molecules in the cluster is

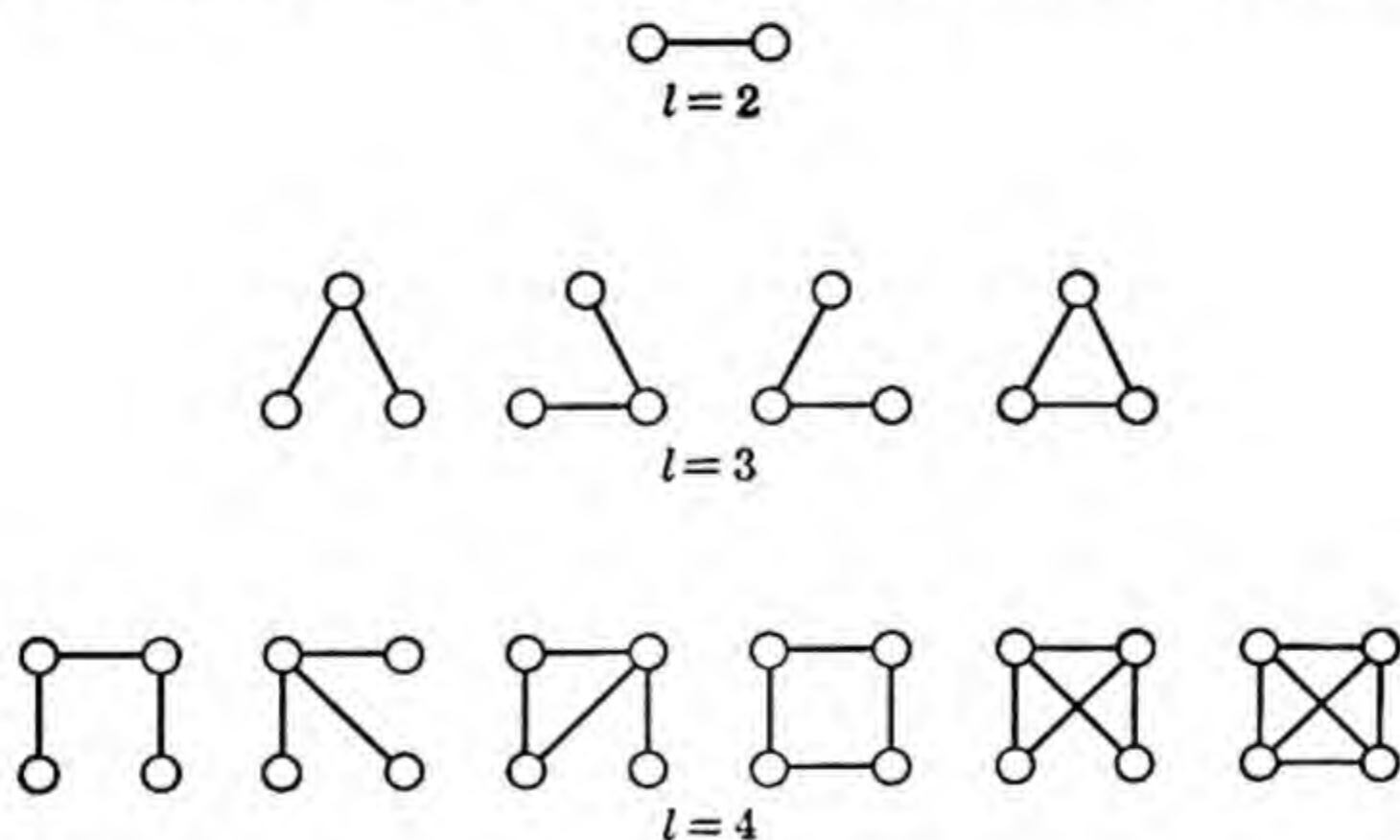


FIG. 55. Types of molecular clusters

indicated by the letter l , and it is the practice to speak of a cluster of l molecules. A single molecule does not, strictly, constitute a cluster within the scope of the definition, but for the sake of completeness such a molecule, which is sufficiently far from all other molecules so as not to interact with them, is referred to as a cluster for which l is equal to unity. If a small circle is used to represent a molecule, and a line joining two circles implies

¹⁵ Mayer, *et al.*, *J. Chem. Phys.*, 5, 67, 74 (1937); 6, 87, 101 (1938); 7, 1019, 1025 (1939); 9, 2, 626 (1941); ref. 1, Chapters 13 and 14; see also, Born and Fuchs, *Proc. Roy. Soc., A*, 166, 391 (1938); Fuchs, *ibid.*, 179, 194 (1941); Kahn and Uhlenbeck, *Physica*, 5, 399 (1938); Frenkel *J. Chem. Phys.*, 7, 200, 538 (1939).

that the molecules are close enough to interact, their mutual potential energy being different from zero, the various types of clusters can then be depicted diagrammatically as in Fig. 55. For a cluster of two molecules, there is only one possibility of interaction. For a cluster of three molecules there are four possibilities, of which three are equivalent and one different; there are thus two types of clusters involving three molecules. If four molecules constitute a cluster, there are many possibilities which fall into several types; some of these are shown in Fig. 55. In a gas, clusters of all sizes, from $l = 1$ to $l = N$, where N is the total number of molecules, will occur. If m_l represents, in general, the numbers of clusters of l molecules each, then the total number of molecules N is the sum of the product of the number l in a cluster and the number m_l of such clusters; thus

$$N = \sum_{l=1}^N l m_l. \quad (71.1)$$

Since two molecules in different clusters do not interact, their coordinates are independent of each other; hence the configuration integral will contain a series of terms, each of which is determined by the molecules in the same cluster.

71b. Cluster Integrals and Irreducible Integrals.—In following up these arguments, it is convenient to introduce, for a cluster of the same l molecules, a quantity called the *cluster integral*. It is given the symbol b_l , and is represented by

$$b_l = \frac{1}{l!V} \int \cdots \int \sum_{\substack{l \geq i, \\ j \geq 1}} \prod f_{ij} d\tau_1 \cdots d\tau_l, \quad (71.2)$$

where f_{ij} is defined, as before, by equation (67.30), viz.,

$$f_{ij} = f(r_{ij}) = e^{-u(r_{ij})/kT} - 1, \quad (71.3)$$

and $d\tau_k$ is employed for brevity in place $dx_k dy_k dz_k$, i.e.,

$$d\tau_k = dx_k dy_k dz_k. \quad (71.4)$$

The summation is taken over all the products of the f_{ij} terms for connected pairs of molecules that can take part in a cluster of the same l molecules. The factor $1/l!V$ in equation (71.2) is introduced for normalization purposes; this makes the cluster integral have the dimensions of V^{l-1} , where V is the volume of the whole system.

For $l = 1$, the cluster integral is

$$b_1 = \frac{1}{V} \int d\tau_1 = 1, \quad (71.5)$$

which is equal to unity, since integration over the coordinates of the molecules gives simply the volume of the containing vessel.

The cluster integral for $l = 2$, is

$$\begin{aligned} b_2 &= \frac{1}{2V} \int \int f_{12} d\tau_1 d\tau_2 \\ &= \frac{1}{2V} \int \int \{e^{-u(r_{12})/kT} - 1\} d\tau_1 d\tau_2. \end{aligned} \quad (71.6)$$

Upon carrying out the integration over the coordinates of the molecule 2, by the method described in Section 67e, the result is given by equation (67.35) as β ; thus,

$$\begin{aligned} \int f_{12} d\tau_2 &= \int \int \int \{e^{-u(r_{12})/kT} - 1\} dx_2 dy_2 dz_2 \\ &= \beta. \end{aligned} \quad (71.7)$$

Further, integration over the coordinates of the molecule 1 gives V , so that

$$b_2 = \frac{1}{2V} \times \beta_1 V = \frac{1}{2} \beta_1, \quad (71.8)$$

where the subscript 1 has been added to β , i.e., β_1 , in order to identify it as the first of the analogous (irreducible) integrals for which the general symbol β_s will be used, as explained below.

When the cluster contains three molecules, i.e., $l = 3$, the corresponding cluster integral is given by (cf. Fig. 55)

$$b_3 = \frac{1}{6V} \int \int \int (f_{12}f_{31} + f_{23}f_{31} + f_{23}f_{21} + f_{12}f_{23}f_{31}) d\tau_1 d\tau_2 d\tau_3. \quad (71.9)$$

In the first term of the integral, i.e., $f_{12}f_{31}$, the coordinates of molecule 3 occur only in f_{31} ; hence, integration of this term over the coordinates of this molecule gives

$$\int f_{31} d\tau_3 = \beta_1,$$

which is equal to β_1 , as may be seen from the results given above for the $l = 2$ cluster. Similarly, integration of the same term over the coordinates of molecule 2, i.e.,

$$\int f_{12} d\tau_2 = \beta_1,$$

also leads to β_1 , while integration over the coordinates of the last particle, i.e., over $d\tau_1$, gives the volume V . It follows, therefore, that

$$\int \int \int f_{12}f_{31} d\tau_1 d\tau_2 d\tau_3 = V\beta_1^2. \quad (71.10)$$

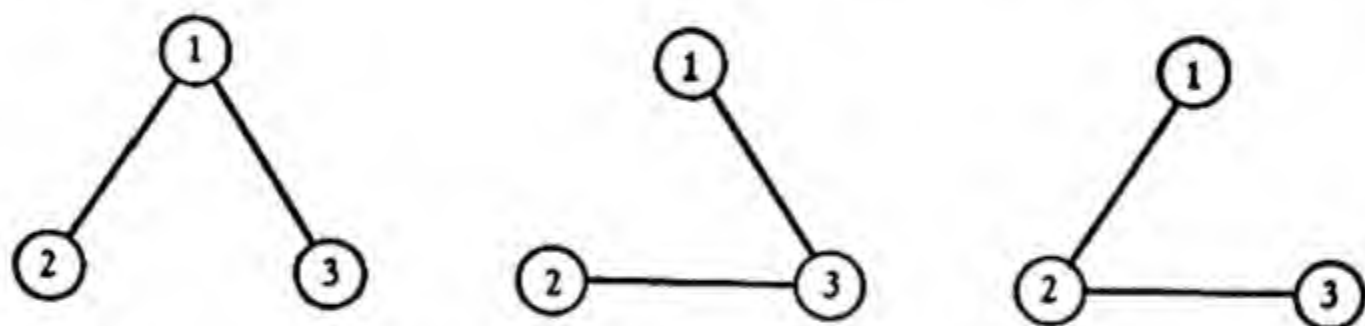
The second and third terms in the integration of equation (71.9) evidently lead to the same result, so that the first three terms contribute $3V\beta_1^2$ to the integral. The last term in equation (71.9) cannot be simplified further, and its value is therefore defined in terms of a quantity β_2 , called the second *irreducible integral*, β_1 being the first; thus,

$$\beta_2 = \frac{1}{2V} \iiint f_{12}f_{23}f_{31}d\tau_1d\tau_2d\tau_3. \quad (71.11)$$

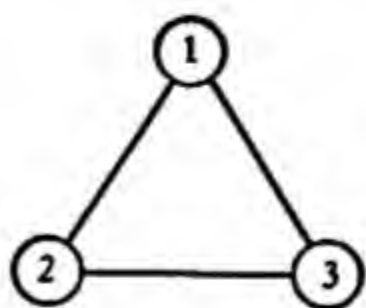
Combination of equation (71.11) with (71.9) and (71.10), gives

$$\begin{aligned} b_3 &= \frac{1}{6V} (3V\beta_1^2 + 2V\beta_2) \\ &= \frac{1}{2}\beta_1^2 + \frac{1}{3}\beta_2. \end{aligned} \quad (71.12)$$

Proceeding in this manner, it is possible to derive expressions for the cluster integrals corresponding to all values of l ; for this purpose, however, it is convenient to consider the general form of the irreducible clusters and the corresponding irreducible integrals. It was seen that the terms $f_{12}f_{31}$, $f_{23}f_{31}$ and $f_{23}f_{21}$, in the expression (71.9) for b_3 , could be reduced to the product of two independent factors, each involving a pair of molecules; the clusters represented by



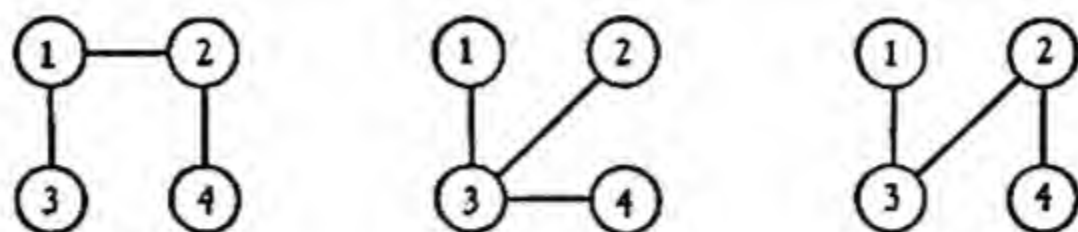
are thus reducible, and the corresponding integrals are reducible integrals. The integral for the cluster



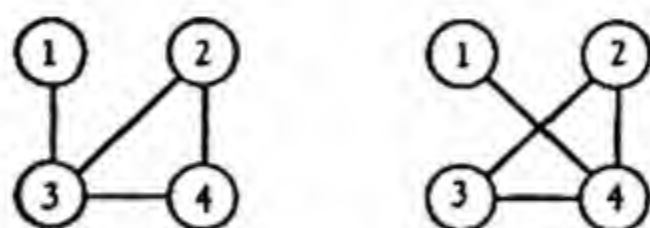
cannot, however, be factorized into the product of simpler integrals; hence, this integral is irreducible, and is defined by equation (71.11) as $2V\beta_2$. The essential difference between a reducible and an irreducible cluster is that in the former one or more of the molecules interact with, i.e., is connected with, but one molecule, while in the latter every molecule interacts with at least two others.¹⁶ Applying these considerations, it is seen that in the cluster

¹⁶ The cluster with two molecules is, of course, irreducible, although it is an apparent exception to the rule given here.

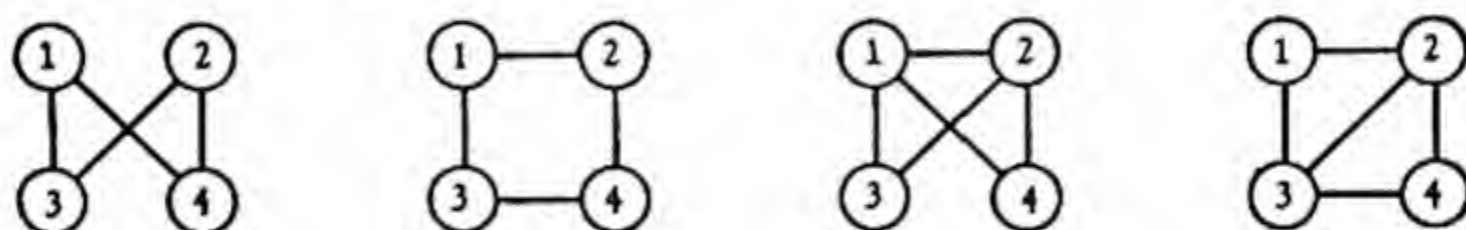
for which l is 4, the contributions to the cluster integral b_4 of the configurations



are reducible to powers of β_1 . Similarly, the terms for the clusters



are reducible to those whose integrals are given in terms of β_1 and β_2 . The other clusters involving four molecules, such as



are irreducible, for in these arrangements every molecule interacts with at least two others, as is indicated by the connecting lines. The contributions of these clusters, ten in all, are irreducible, and they are included in the irreducible integral β_3 .

The irreducible integrals can be expressed in terms of a general formula; this is based on the fact that, apart from the normalizing factor $1/s!V$, the irreducible integral β_s is the integral over the configuration space of the $s + 1$ molecules. The integrand is the sum of all products of the f_{ij} terms of $s + 1$ molecules which cannot be further reduced to a product of integrals. The general definition is then

$$\beta_s = \frac{1}{s!V} \int \cdots \int \sum_{\substack{s+1 \geq i, \\ j \geq 1}} \prod f_{ij} d\tau_1 \cdots d\tau_{s+1}, \quad (71.13)$$

where the summation is restricted to the f_{ij} products for all the irreducible clusters of the same $s + 1$ molecules.

It is evident from the foregoing considerations that every cluster integral b_l may be stated as the sum of terms, each of which contains one or more irreducible integrals; thus, the first four cluster integrals are

$$\begin{aligned} b_1 &= 1 \\ b_2 &= \frac{1}{2}\beta_1 \\ b_3 &= \frac{1}{2}\beta_1^2 + \frac{1}{3}\beta_2 \\ b_4 &= \frac{2}{3}\beta_1^3 + \beta_1\beta_2 + \frac{1}{4}\beta_3. \end{aligned}$$

The general expression for b_l can, in fact, be shown to be

$$b_l = \frac{1}{l!} \sum_{n_s} \prod_s \frac{(l\beta_s)^{n_s}}{n_s!} \quad (71.14)$$

where

$$\sum_{s=1}^{l-1} sn_s = l - 1, \quad (71.15)$$

the symbol n_s being the power with which β_s occurs in any term of b_l .

71c. Evaluation of the Configuration Integral.—Having thus defined the cluster integrals in terms of the simple irreducible integrals, attention can now be turned to the problem of the configuration integral for the system. As already noted, the latter involves a series of products of integrals, each of which is concerned only with molecules in the same cluster. It is evidently possible to express the configuration integral in terms of the cluster integrals, and hence in terms of the irreducible integrals. The result is

$$Q_u = N! \sum_{m_l} \prod_l \frac{(Vb_l)^{m_l}}{m_l!}, \quad (71.16)$$

where, as noted in equation (71.1), the sum of all the lm_l terms is equal to N . In deriving this expression the cluster integral is regarded as independent of volume; such is undoubtedly the case provided the volume is not too small or l , the number of molecules in the cluster, is not too large. The consequence of the failure of these conditions to hold will be considered later.

In order to simplify the equation (71.16) for the configuration integral, the device is adopted of substituting the logarithm of the largest term for the logarithm of the sum; under the given conditions the difference is not significant. This approximation leads to the result

$$\ln \frac{Q_u}{N!} = N \sum_{l=1}^{\infty} vb_l Z^l - N \ln Z, \quad (71.17)$$

where Z is determined by

$$\sum_{l=1}^{\infty} l vb_l Z^l = 1, \quad (71.18)$$

v being equal to V/N , the volume per single molecule. The solution of equation (71.18) can best be achieved by writing Z as a series involving inverse powers of v ; this can be done provided the terms in the summation (71.18) converge as l increases, as is the case when the gas density is not too great. Corresponding expressions can be written for Z^2 , Z^3 , Z^4 , etc., and the coefficients of the powers of v^{-1} can then be evaluated in terms of b_1 , b_2 , etc., by means of equation (71.18). If these are then converted into the

corresponding β_1, β_2 , etc., it is found that

$$Z = \frac{1}{v} e^{-\sum \beta_s v^{-s}}, \quad (71.19)$$

and hence

$$\ln Z = -\ln v - \sum_{s \geq 1} \beta_s v^{-s}. \quad (71.20)$$

In a similar manner it can be shown that

$$\sum_{l \geq 1} v b_l Z^l = 1 - \sum_{s \geq 1} \frac{s}{s+1} \beta_s v^{-s}. \quad (71.21)$$

Combination of equations (71.20) and (71.21) with (71.17) then gives

$$\begin{aligned} \ln \frac{Q_u}{N} &= N \left(1 - \sum_{s \geq 1} \frac{s}{s+1} \beta_s v^{-s} + \sum \beta_s v^{-s} + \ln v \right) \\ &= N \left(1 + \sum_{s \geq 1} \frac{1}{s+1} \beta_s v^{-s} + \ln v \right). \end{aligned} \quad (71.22)$$

71d. Equation of State.—From this result the complete partition function, or rather its logarithm, can be obtained in the usual manner, and hence expressions for the thermodynamic properties of the imperfect gas can be derived. The general equation of state, for example, is given by

$$\begin{aligned} P &= kT \left(\frac{\partial \ln Q_u}{\partial V} \right)_T = \frac{kT}{N} \left(\frac{\partial \ln Q_u}{\partial v} \right)_T \\ &= \frac{kT}{v} \left(1 - \sum_{s \geq 1} \frac{s}{s+1} \beta_s v^{-s} \right) \\ &= \frac{NkT}{V} \left(1 - \sum_{s \geq 1} \frac{s}{s+1} \beta_s v^{-s} \right). \end{aligned} \quad (71.23)$$

The difficulty in applying this equation, and others of a similar type, lies in the evaluation of the cluster integrals β_s . However, it is of interest to investigate equation (71.23) under some simple conditions; for example, at very low pressures v is large, and hence the term involving v^{-s} is negligible. The gas then satisfies the relationship $P = NkT/V$, as is to be expected. If clusters are restricted to those consisting of one or two molecules only, i.e., the maximum value of l is 2, then the maximum value of s will be 1, and equation (71.23) becomes

$$\begin{aligned} P &= \frac{NkT}{V} \left(1 - \frac{1}{2} \beta_1 \frac{1}{v} \right) \\ &= \frac{NkT}{V} \left(1 - \frac{1}{2} \beta_1 \frac{N}{V} \right). \end{aligned} \quad (71.24)$$

Since β_1 has the same significance as β , this equation is identical with equation (68.2).

Expanding the summation in equation (71.23), the general equation of state becomes

$$P = \frac{NkT}{V} \left\{ 1 - \frac{1}{2}\beta_1 \left(\frac{N}{V} \right) - \frac{2}{3}\beta_2 \left(\frac{N}{V} \right)^2 - \frac{3}{4}\beta_3 \left(\frac{N}{V} \right)^3 - \cdots \right\}, \quad (71.25)$$

so that the third virial coefficient is given by

$$C(T) = -\frac{2}{3}\beta_2 N^2, \quad (71.26)$$

while the fourth virial coefficient is

$$D(T) = -\frac{3}{4}\beta_3 N^3.$$

In spite of the difficulties involved, the integral β_2 has been solved and the third virial coefficient of argon has been calculated; the result is in satisfactory agreement with the not too reliable experimental datum.

A highly interesting general conclusion can be drawn from a comparison of equations (71.23) and (71.21); it is seen that

$$P = \frac{kT}{v} \sum v b_l Z^l. \quad (71.27)$$

Upon multiplying both sides of equation (71.18) by N , the result is

$$N \sum l v b_l Z^l = N, \quad (71.28)$$

and since by equation (71.1)

$$\sum l m_l = N, \quad (71.29)$$

it follows on the basis of a term by term correspondence between (71.28) and (71.29), that

$$\sum m_l = N \sum v b_l Z^l.$$

Insertion of this result in equation (71.27) then gives

$$P = \frac{kT}{V} \sum m_l, \quad (71.30)$$

where V is written in place of Nv . For an ideal gas, $P = NkT/V$, and hence $\sum m_l$, the total number of clusters in an imperfect gas, takes the place of N the total number of molecules. It is seen, therefore, that each cluster in an imperfect gas has the same influence in determining the pressure as does a single molecule in a perfect gas. The pressure of a real gas will thus be the same as that of an ideal gas containing the same number of molecules as the real gas has clusters, irrespective of their size.

71e. Activity Coefficient of a Gas.—The free energy of one mole of a gas is given by

$$\begin{aligned} F &= -kT \ln Q + PV \\ &= -kT \ln \frac{1}{N!} \left\{ \frac{(2\pi mkT)^{3/2}}{h^3} \right\}^N Q_u Q_i + PV \\ &= -NkT \ln \frac{(2\pi mkT)^{3/2}}{h^3} Q_i - kT \ln \frac{Q_u}{N!} + PV. \end{aligned}$$

Upon introducing the value of $\ln Q_u/N!$ given by equation (71.22) and that of PV from equation (71.23), it is seen that

$$F = -NkT \left\{ \ln \frac{(2\pi mkT)^{3/2}}{h^3} Q_i + \ln v + \sum \beta_s v^{-s} \right\},$$

and hence, utilizing equation (71.20),

$$F = -NkT \left\{ \ln \frac{(2\pi mkT)^{3/2}}{h^3} \cdot \frac{Q_i}{Z} \right\}. \quad (71.31)$$

For an ideal gas,

$$\begin{aligned} F &= -NkT \ln \frac{Q}{N} \\ &= -NkT \left\{ \ln \frac{(2\pi mkT)^{3/2}}{h^3} \cdot \frac{V}{N} Q_i \right\}, \end{aligned} \quad (71.32)$$

and comparison of equations (71.31) and (71.32) shows that Z^{-1} is the equivalent of V/N , the volume per single molecule in an ideal gas. It follows, therefore, that Z is the activity of the real gas in terms of the standard state of an ideal gas at a concentration of one molecule per cc., assuming V to be expressed in cubic centimeters. The product Zv is the activity coefficient γ for the same standard state, so that

$$\gamma = Zv = e^{-\sum \beta_s v^{-s}}. \quad (71.33)$$

71f. Statistical Mechanics of Condensation.—The equations derived in the foregoing sections have been based on two postulates; first, that the cluster integrals b_l are independent of the volume, and second, that the function $lvb_l Z^l$ becomes vanishingly small for large l values, so that Z can be expressed as a series of inverse powers of v . There are circumstances in which these assumptions are not justifiable, namely when the volume is small or when there are clusters with large numbers of molecules, respectively. These are just the conditions under which condensation of the gas to form a liquid is to be expected, and it will be shown that a consideration of the statistical mechanical equations leads to this very conclusion. The remarkable achievement of the present approach to the problem of condensation, as compared with all others, is that it requires a region of constant pressure, with changing volume, in the P - V isothermal, such as is actually observed in the course of condensation.

The definition of b_l given by equation (71.14) holds for all values of l , but when l is very large this form is not practical for the evaluation of b_l ; in these circumstances, however, it is possible to write

$$\ln b_l = l \left(\sum_{s=1}^{l-1} \beta_s \rho^s - \ln \rho \right), \quad (71.34)$$

where ρ is defined by

$$\sum_{s=1}^{l-1} s \beta_s \rho^s = 1. \quad (71.35)$$

Strictly speaking, equation (71.34) gives the limiting value of b_l as l approaches infinity; since $\ln b_l$ is evidently proportional to l , it is possible to define a quantity $\ln b_0$ as l^{-1} times this limit, so that

$$\ln b_0 = \sum_{s=1}^{l-1} \beta_s \rho^s - \ln \rho, \quad (71.36)$$

and consequently

$$\lim_{l \rightarrow \infty} \ln b_l = l \ln b_0. \quad (71.37)$$

In general $\ln b_l$ may differ from $l \ln b_0$, and the difference depends on both the value of l and of the irreducible integrals β_s ; the exact nature of this difference is not significant, but it may be represented by the function $\ln f(l, \beta)$. Hence,

$$\ln b_l = l \ln b_0 + \ln f(l, \beta), \quad (71.38)$$

and an exact equation, applicable for all l values, is

$$b_l = b_0^l f(l, \beta). \quad (71.39)$$

Since $\ln b_l$ becomes equal to $l \ln b_0$ in the limit as l increases, it is evident from equation (71.38) that $\ln f(l, \beta)$ must then approach zero; this condition can be represented by

$$\lim_{l \rightarrow \infty} l^{-1} \ln f(l, \beta) = 0. \quad (71.40)$$

According to equation (71.18), it is always true that

$$\sum_{l=1}^N l v b_l Z^l = 1, \quad (71.41)$$

and hence by equation (71.39),

$$\sum_{l=1}^N l v (b_0 Z)^l f(l, \beta) = 1,$$

$$\therefore \sum_{l=1}^N l (b_0 Z)^l f(l, \beta) = v^{-1} \quad (71.42)$$

It is now of interest to see from this equation how v^{-1} varies as Z increases; when Z is zero, the value of v^{-1} is obviously also zero, but the latter increases as Z increases. In the summation represented by equation (71.42), the first term, i.e., for $l = 1$, is always equal to Z since b_1 is unity; this result may be easily derived directly from equation (71.41). Provided Z is small, the second and subsequent terms in equation (71.42) are negligible, and hence for small values of Z , it appears that Z is always equal to v^{-1} . The plot of Z against v^{-1} , as derived from equation (71.42), is thus, under these conditions, a straight line, of slope 45° , passing through the origin (Fig. 56). As Z increases, the second and higher terms in the summation of equation (71.42), which are all positive, begin to make appreciable contributions and then v^{-1} increases more rapidly than does Z . The effect is not large, however, until a certain value of Z is reached when terms involving large l 's begin to contribute very markedly to the sum; this occurs when Z is equal to b_0^{-1} , and beyond that point v^{-1} increases with such enormous rapidity that the curve is practically vertical, as shown in Fig. 56.

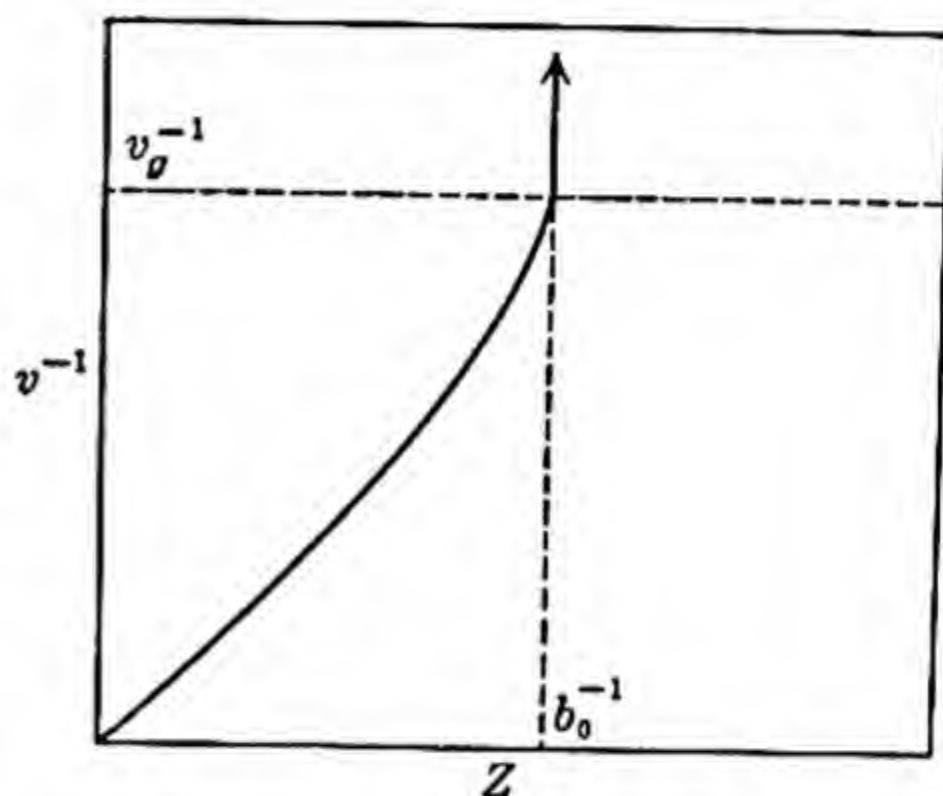


FIG. 56. Statistical mechanics of condensation

The following general considerations may prove of value in understanding the situation. When l is very large, e.g., of the order of 10^{23} , as is possible in a mole of gas, since l can take all values from unity to N , the function $f(l, \beta)$ will approach unity, according to the limitation expressed by equation (71.40); under these conditions, equation (71.42) becomes

$$\sum_{l=1}^N l(b_0 Z)^l \approx v^{-1}. \quad (71.43)$$

Consider the last term in this summation, i.e., $N(b_0 Z)^N$; as long as $b_0 Z$ is less than unity, $(b_0 Z)^N$ will be very small, since N is very large, and this term will make a negligible contribution to the sum of equation (71.43). However, as soon as $b_0 Z$ just exceeds unity, the contribution of the N th term becomes extremely large, and the same will be true of other terms for which l is large. It is evident, therefore, that the sums represented by equations (71.42) and (71.43) will increase with great rapidity when $b_0 Z$ becomes unity; hence the value of v^{-1} will rise very sharply at the point for which Z is equal to b_0^{-1} . The value of v^{-1} at this point is represented by v_0^{-1} , and it will be seen shortly that v_0 is the volume per molecule in the saturated vapor.

It is of interest to consider the results depicted in Fig. 56 from another standpoint. It has been seen that Z may be identified with the activity of

the gas, with the standard state that of the ideal gas at a concentration of v^{-1} , i.e., one molecule per unit volume. According to Fig. 56, Z is equal to v^{-1} for low values of v^{-1} , i.e., at low densities; the activity is then equal to the concentration, as is to be expected. As the density increases, the activity falls below the concentration, and the activity coefficient is less than unity because of appreciable departure from ideal behavior. When condensation sets in the activity coefficient of the system, with reference to the gaseous state, decreases rapidly.

It would appear from the previous arguments that v^{-1} increases to infinity just beyond the point at which Z is equal to b_0^{-1} ; in other words, it might seem that for all values of v^{-1} in excess of v_0^{-1} the solution for Z is b_0^{-1} . This is, however, not the case, for at small values of v , i.e., when v^{-1} is large, one of the limitations referred to at the beginning of this section begins to operate. At a certain value of v , referred to as v_f , which is the volume per molecule in the liquid (fluid) state, b_l is no longer independent of the volume, and then $b_0 Z$ is no longer equal to unity. It follows, therefore, that Z is equal to b_0^{-1} for all values of v , only if the latter lie within the range of v_0 to v_f ; that is

$$b_0 Z = 1 \quad \text{for} \quad v_f \leq v \leq v_0, \quad (71.44)$$

or, from equation (71.36),

$$\ln Z = \ln \rho - \sum_{s \geq 1} \beta_s \rho^s \quad \text{for} \quad v_f \leq v \leq v_0. \quad (71.45)$$

71g. Constancy of Free Energy in the Condensation Range.—The equation (71.7) for the logarithm of the configuration integral, viz.,

$$\ln \frac{Q_u}{N!} = N(\sum v b_l Z^l - \ln Z), \quad (71.46)$$

is applicable to all volumes v , and hence the pressure P can be expressed by

$$\begin{aligned} P &= \frac{kT}{N} \left(\frac{\partial \ln Q_u}{\partial v} \right)_T \\ &= \frac{kT}{v} \left\{ \sum v b_l Z^l - (\sum l v b_l Z^l - 1) \left(\frac{\partial \ln Z}{\partial \ln v} \right)_T \right\}. \end{aligned} \quad (71.47)$$

Since $\sum l v b_l Z^l$ is equal to unity, by equation (71.41), it follows that

$$P = \frac{kT}{v} \sum v b_l Z^l \quad (71.48)$$

$$= \frac{NkT}{V} \sum v b_l Z^l. \quad (71.49)$$

Differentiation of equation (71.48) or (71.49) with respect to V gives

$$\begin{aligned} V \left(\frac{\partial P}{\partial V} \right)_T &= kTv \left\{ \frac{\partial (\sum v b_i Z^i)}{\partial v} \right\}_T \\ &= \frac{kT}{v} \sum l v b_i Z^i \left(\frac{\partial \ln Z}{\partial \ln v} \right)_T \\ &= \frac{kT}{v} \left(\frac{\partial \ln Z}{\partial \ln v} \right)_T, \end{aligned} \quad (71.50)$$

since $\sum l v b_i Z^i$ is equal to unity. From the latter fact, it also follows that the derivative of this quantity with respect to $\ln v$ must be zero, so that

$$\begin{aligned} \left\{ \frac{\partial (\sum l v b_i Z^i)}{\partial \ln v} \right\}_T &= \sum l v b_i Z^i + \sum l^2 v b_i Z^i \left(\frac{\partial \ln Z}{\partial \ln v} \right)_T \\ &= 0, \\ \therefore \left(\frac{\partial \ln Z}{\partial \ln v} \right)_T &= - \frac{1}{\sum l^2 v b_i Z^i}. \end{aligned} \quad (71.51)$$

Substitution of this result into equation (71.50) then gives

$$V \left(\frac{\partial P}{\partial V} \right)_T = - \frac{kT}{v} \cdot \frac{1}{\sum l^2 v b_i Z^i}. \quad (71.52)$$

In the volume range between v_0 and v_f , the sum $\sum l b_i Z^i$, which is equivalent to that in equation (71.42), contains terms of very large value, as seen above; hence the summation in the denominator of equation (71.52) must be extremely large in the specified volume range. It follows, therefore, that

$$V \left(\frac{\partial P}{\partial V} \right)_T \approx 0$$

in the range between v_0 and v_f , and hence the pressure remains constant irrespective of volume changes, at constant temperature. This is, of course, one of the essential characteristics of a condensing system, and hence the range between v_0 and v_f may be referred to as the condensation range.

Utilizing results already derived, it is a simple matter to prove that the free energy of the system remains constant in the condensation range. According to equation (71.31),

$$F = - RT \left\{ \ln \frac{(2\pi m k T)^{3/2}}{h^3} \cdot \frac{Q_i}{Z} \right\},$$

but provided the volume lies between v_f and v_0 , the value of Z is virtually constant, and equal to b_0^{-1} . It follows, therefore, that the free energy is constant and independent of the volume in the condensation range.

Upon differentiation of equation (71.23) for the pressure with respect to $\ln V$, the result is

$$\begin{aligned} \left(\frac{\partial P}{\partial \ln V} \right)_T &= V \left(\frac{\partial P}{\partial V} \right)_T \\ &= - \frac{kT}{v} \left(1 - \sum_{s \geq 1} s \beta_s v^{-s} \right). \end{aligned} \quad (71.53)$$

In the condensation range this must be zero, and hence under these conditions

$$\sum s \beta_s v^{-s} = 1. \quad (71.54)$$

It is evident that the largest positive root v of this equation is equal to v_0 , since it is known (cf. Fig. 56) that v_0^{-1} is the smallest value of the parameter v^{-1} at which condensation commences. Actually it can be shown that v_0^{-1} is the only real positive root of equation (71.54), and so it may be taken as defining the volume of the system when condensation begins. It can be concluded therefore that, in general, as the summation represented by the left-hand side of equation (71.54) increases, with increasing v^{-1} , condensation commences, i.e., v is equal to v_0 , when the sum becomes equal to unity.

71h. The Critical State.—An examination of the variation of the summation $\sum s \beta_s v^{-s}$, with respect to the reciprocal volume v^{-1} , at a series of temperatures in the condensation range, brings to light some interesting facts relating to the critical state. For this purpose it is desirable to know something, in the first place, concerning the variation of the irreducible integrals β_s [equation (71.13)] with the temperature. These integrals have been evaluated for low values of s , and the conclusions drawn are probably of general applicability. It appears that at temperatures lower than those in the neighborhood of the critical point, all the β_s 's are positive; at higher temperatures, the β_s 's decrease and finally become negative, but the temperatures at which the change occurs are higher the smaller the value of s .

At low temperatures, when all the β_s 's are positive, equation (71.54) has only one real positive root, and this is equal to v_0 . As the temperature increases, however, some of the irreducible integrals β_s , with higher s values, become negative, and a point is reached at which equation (71.54) has no positive root. At higher temperatures, therefore, there is no volume v_0 for which $(\partial P / \partial V)_T$ becomes zero; in other words, above a certain temperature condensation is no longer possible, and hence this must represent the critical point. The conclusions may be depicted graphically by plotting the values of $\sum s \beta_s v^{-s}$ against v^{-1} for a series of temperatures, as in Fig. 57. At temperatures above the critical point the curves are of the type VI, which never attains the value of unity because of the influence of the higher (negative) β_s 's; at such temperatures there is consequently no condensation. Since the ordinate of curve VI in Fig. 57 never reaches unity, it is evident from equation (71.53) that $(\partial P / \partial V)_T$ is always negative; thus the volume decreases continuously with increasing pressure, as is characteristic of the gaseous state.

As the temperature is decreased, a point is reached (curve V) at which the maximum value of the summation just attains unity, and condensation is just possible; this, of course, occurs at the critical temperature. For temperatures above the critical point, the curve IV crosses the line for which $\sum s\beta_s v^{-s}$ is equal to unity, and hence condensation can occur. A remarkable conclusion to be drawn from the results, however, is that the usual phenomena associated with condensation do not actually manifest themselves until the temperature is below that of a second characteristic temperature, indicated by T_m (curve II).

It will be apparent, from general considerations, that under suitable conditions the plot of $\sum s\beta_s v^{-s}$ against v^{-1} (Fig. 57) will have similar proper-

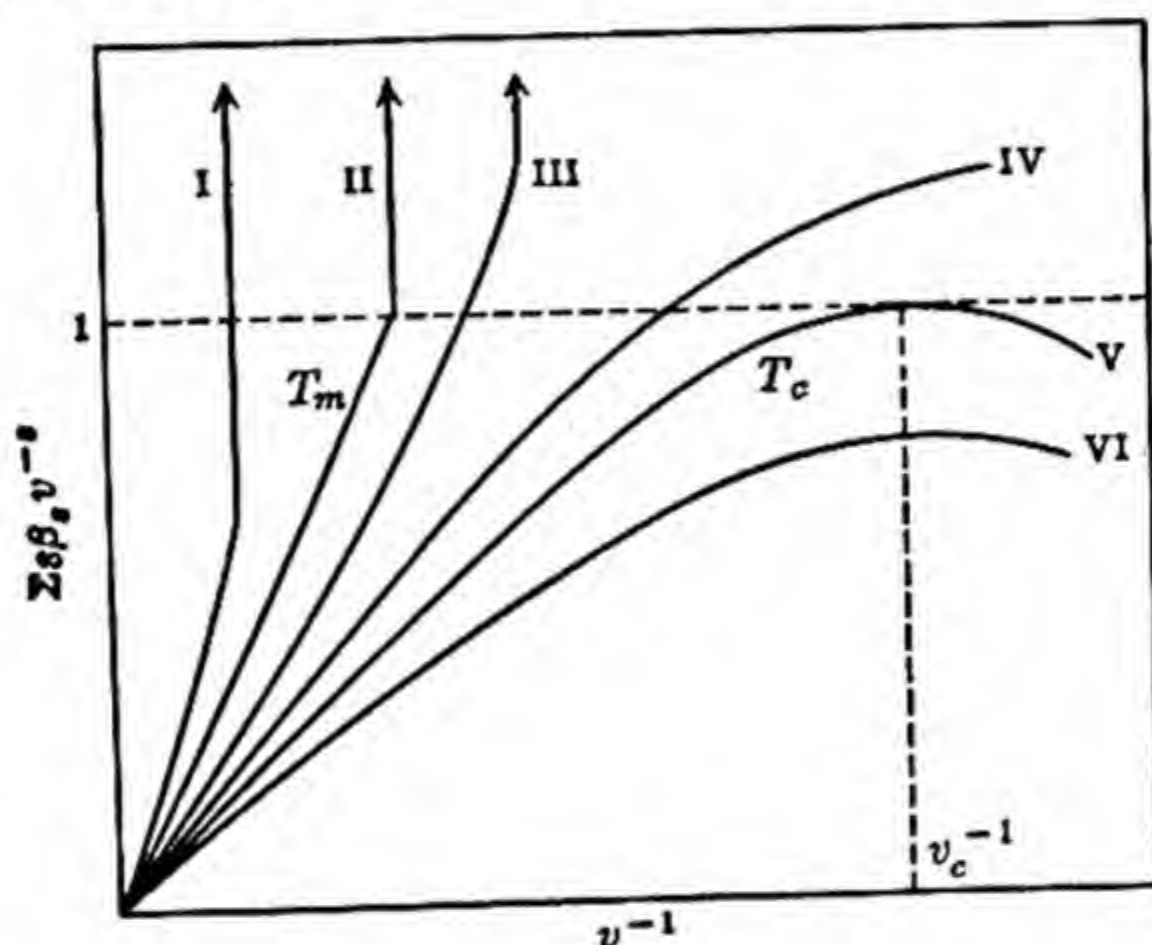


FIG. 57. Theory of the critical state

ties to the curve of Fig. 56, which is the plot of v^{-1} , equal to $\sum lb_i Z^i$, against Z . In the latter case it was seen that when Z attained a particular value, such that $b_0 Z$ was equal to unity, the value of the ordinate increased very sharply. A similar effect is evident in the plots of Fig. 57, when the temperatures are in the vicinity of the characteristic temperature T_m ; the value of the ordinate increases rapidly at the volume for which

$$\beta_0 v^{-1} = 1,$$

i.e., for which $v = \beta_0$, where β_0 is defined, by analogy with b_0 [cf. equation (71.37)] as

$$\lim_{s \rightarrow \infty} \ln \beta_s = s \ln \beta_0,$$

the value of β_0 decreasing with increasing temperature. If the temperature is just above T_m , as in curve III, the sum $\sum s\beta_s v^{-s}$ is greater than unity when v becomes equal to β_0 , i.e., when the curve becomes almost vertical. The sudden increase in the ordinate does not occur, therefore, until v^{-1} is appreci-

ably greater than β_0^{-1} at that temperature, that is, until the volume is less than the value at the condensation point.

From equation (71.53), the slope $(\partial P/\partial V)_T$ is seen to be determined essentially by $\sum s\beta_s v^{-s}$; this slope becomes zero, i.e., condensation occurs, when the summation is equal to unity. It is evident that at a temperature giving a curve of the type III, the value of $\sum s\beta_s v^{-s}$ will approach unity, and hence the slope $(\partial P/\partial V)_T$ will become zero, in a gradual manner; in other words, the slope of the isothermal is continuous through the point at which the volume is v_0 (Fig. 58). This is, of course, quite different from the

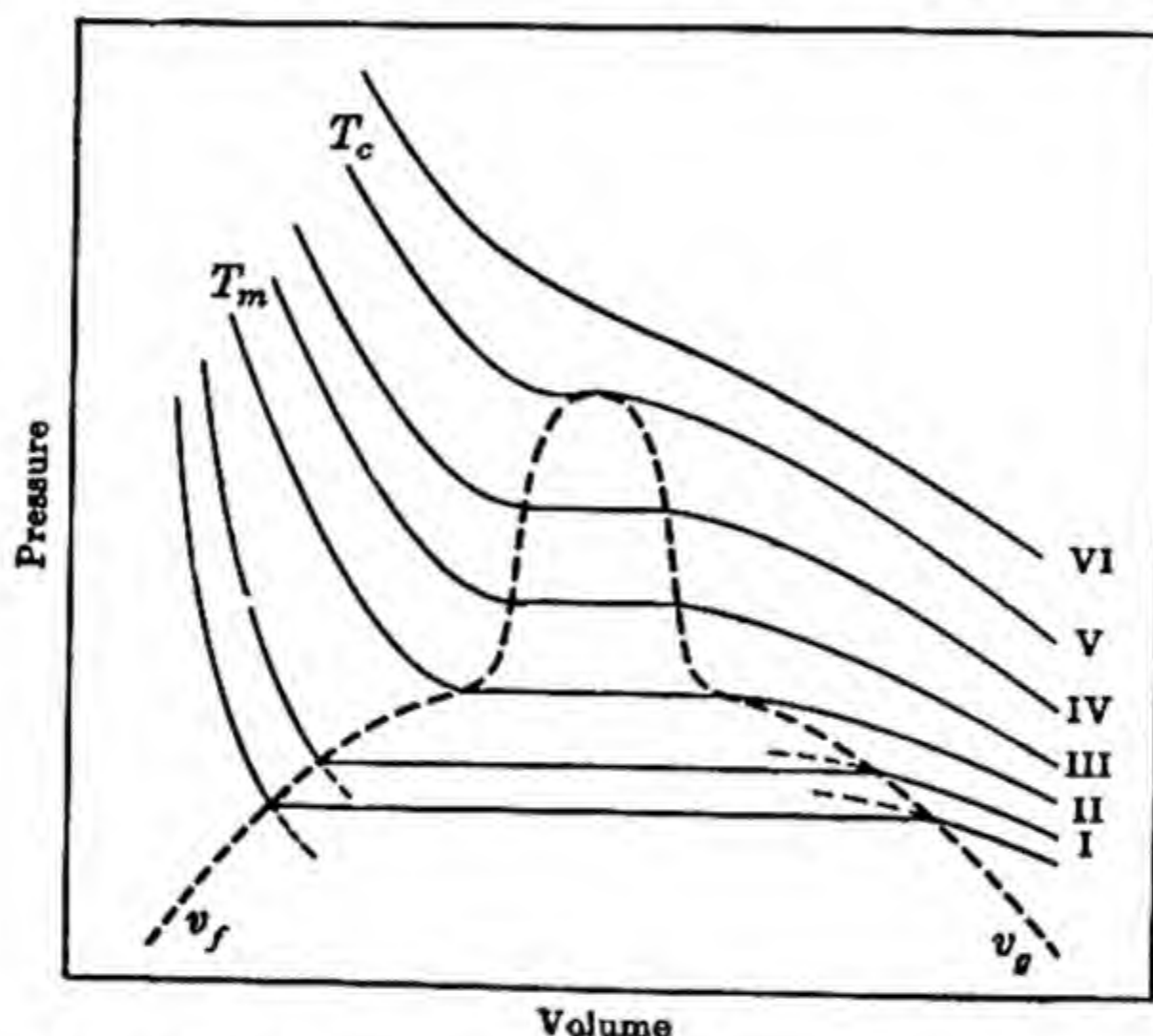


FIG. 58. Pressure-volume isotherms in critical region

familiar behavior associated with condensation; the sharp separation into two phases would require that $(\partial P/\partial V)_T$ should suddenly become zero. When the temperature is equal to T_m or less, so that the curves are of type II or I, respectively, it is seen that the summation $\sum s\beta_s v^{-s}$ starts to increase with great rapidity when it is still less than unity, and its attainment of this value, when the volume is equal to v_0 , is very sudden. It follows, therefore, that at those temperatures the slope $(\partial P/\partial V)_T$ of the isothermal is discontinuous through v_0 , and true condensation, involving separation into two phases, occurs.

According to these arguments, there should be a range of temperature for every gas between T_c and T_m , which may be called the *critical region*; above the temperature T_c the existence of a liquid phase is impossible, whereas separation into two phases will occur only at temperatures below T_m . Between T_c and T_m the system probably consists of a number of medium sized clusters, but there is no tendency for them to be replaced by one very large cluster such as would be characteristic of the liquid phase. It is a striking fact that experimental evidence has existed for some time for just

such a critical region as described here.¹⁷ It has been found that as a liquid is heated, the meniscus disappears at a certain temperature, which would be equal to T_m , but the density does not become uniform, even if the system is stirred. This observation would be in harmony with the presence of moderately large clusters. At a temperature about 10° higher than T_m , the system becomes uniform, and this would presumably be equivalent to T_c .

Attention must be called to the fact that when the ordinates in Fig. 57 exceed the value of unity, i.e., when the volume is smaller than v_0 , many of the equations derived above, which hold only for the gaseous state, are not applicable. This is particularly true for equation (71.23), and for equation (71.53) derived from the former; if $\sum s\beta_i v^{-s}$ were greater than unity, the slope $(\partial P/\partial V)_T$ of the isotherm would be positive, and this is, of course, completely contrary to experience. Further, none of the equations holds when b_i is dependent on v , that is, when the volume is less than that represented by v_f ; in other words, the results are not applicable at all to a system consisting entirely of liquid.

SOLID-LIQUID EQUILIBRIA: FUSION

72a. Order-Disorder Phenomena.—The study of solid-liquid equilibria is not only important because of its bearing on the phenomena associated with melting, but also because it provides another standpoint for a consideration of the liquid state. A satisfactory theory of melting must account for the fact that at constant pressure a solid changes to a liquid at a definite and exact temperature, and not over a range of temperature, and also for the occurrence of a marked volume change at the melting point. A promising solution to the problem is based on the idea of *order-disorder* phenomena, which has been employed with such success to account for the sudden changes in physical properties, such as heat capacity, that have been observed at definite temperatures in certain binary alloys. The crystal lattices of these alloys are such that they can be occupied by either atoms A or B. At relatively low temperatures, however, the A atoms are arranged in a definite manner in one lattice, and so also are the B atoms in an interlocking lattice; this leads to a state of perfect order. At higher temperatures, however, some of the A atoms appear in the B lattice, and vice versa, thus leading to a partial disorder. With increasing temperature the disorder increases, and eventually the A and B atoms are arranged in a completely random manner; the state is then one of perfect, or complete, disorder. In spite of the fact that the transition from complete order to complete disorder is a gradual one, and the lattice structure generally undergoes no particular change, mathematical methods show that a discontinuity in certain properties, notably the heat capacity, is to be expected at a definite temperature, in accordance with observation.

There is clearly a parallelism between order-disorder transitions in alloys and the phenomena of fusion; in the solid (crystalline) state there is complete

¹⁷ Maass and Geddes, *Trans. Roy. Soc., A*, 236, 303 (1937); Maass, *Chem. Rev.*, 23, 17 (1938).

order, whereas a liquid is mainly disordered, although there is evidence of short range order even in liquids. It is of interest, therefore, to see if the methods used to study order-disorder in alloys, where there are two components, can be applied to fusion, where one component only is involved. Considerable success in this direction has been achieved by Lennard-Jones and Devonshire;¹⁸ these authors have used two different mathematical procedures, based on virtually the same model. One of these is more exact, but relatively complicated; the other, simpler, somewhat more approximate, procedure will be described here.

72b. Model of the Process of Fusion.—The model postulated in Section 70a for a highly compressed gas and a liquid, of a molecule moving in the field of force of its neighbors and confined by them to a small region of space, referred to as a cell, is also adopted for the solid state. The essential difference between a solid and a liquid is then that in the former case the cell is localized, whereas in the latter it is not; in other words, in the solid the atom or molecule cannot move from one cell to another, whereas in the liquid it can. In order to permit of this migration from one cell to another, it is necessary to have a suitable mechanism, and it is in this connection that the concept of order-disorder is introduced. In the solid the molecules will occupy, or rather vibrate about, definite sites, such as the points of a face-centered cubic lattice; these will be referred to as α -sites, or normal sites. It is suggested that there are available another set of intermediate sites, known as β -sites, that are symmetrically related to the α -sites. The number of α -sites and of β -sites are supposed to be equal to one another, and to N , the total number of molecules in the system. The arrangement of α - and β -sites may be regarded as equivalent to the interpenetrating face-centered lattices of sodium ions and of chloride ions, such as constitute a crystal of sodium chloride. Just as each sodium ion in the latter is surrounded by six chloride ions, and each chloride ion by six sodium ions, so it is considered that in any system of the face-centered type each α -site will have six adjacent β -sites around it, and that there will be six α -sites around each β -site. At temperatures well below the melting point, practically all the molecules will be in fixed positions and will occupy the normal (α) sites, with very few on the abnormal (β) sites. As the temperature is raised, and particularly in the liquid state, there will be increasing occupation of the β -sites, with the result that the molecules will be able to move more and more freely from one α -site to another, through the intermediacy of the β -sites. The latter thus provide the means whereby migration becomes possible in the liquid state.

When the α -sites are occupied almost exclusively, as in the solid state, the condition is one of complete order, but in the liquid state there is considerable disorder, for both α - and β -sites will be occupied. When there is an equal probability of finding a molecule on a site of either type, the liquid

¹⁸ Lennard-Jones and Devonshire, *Proc. Roy. Soc., A*, 169, 317 (1939); 170, 464 (1939); Lennard-Jones, *Proc. Phys. Soc. (London)*, 52, 729 (1940); see also, Frank, *ibid.*, 170, 182 (1939); Rice, *J. Chem. Phys.*, 7, 138, 883 (1939); 9, 121 (1941); Kirkwood and Monroe, *ibid.*, 9, 514 (1941).

is completely disordered, at least as far as long range order is concerned. In the latter circumstances there will be free interchange of molecules from one normal (α) site to another, and so the characteristic properties of viscosity and diffusion become evident. It is the transition, then, from an ordered arrangement in which all the molecules occupy normal sites, to a state in which the molecules are randomly distributed among normal and abnormal sites, that is the basis of the phenomenon of fusion.

Since the change from order to disorder must inevitably be continuous, it may be wondered how this can lead to a sharp discontinuity, such as is observed in the volume, for example, at the melting point. The reason for this is to be found in the fact that the order-disorder change is cooperative in effect. Because of the repulsive fields of atoms that are in close proximity, the β -sites are states of higher energy, and it would normally require a large amount of energy to remove a single molecule from an α -site and transfer it to a β -site, while all the other molecules remained on α -sites. However, it can be seen that if several molecules near one another changed from α -sites to β -sites simultaneously, the amount of energy required would be considerably diminished. Since less energy is required, therefore, the transition from order to disorder will tend to take place suddenly rather than gradually.

72c. Partition Function for Solid-Liquid System.—According to the model just described, there is one α -site and one β -site per molecule, and the degree of order of any configuration of the system can be described by the number of molecules N_α on the α -sites and the number N_β on the β -sites. If q is used to represent the degree of order, then it may be defined by

$$q = \frac{N_\alpha}{N} \quad (72.1)$$

and

$$1 - q = \frac{N_\beta}{N}, \quad (72.2)$$

$$\therefore \frac{q}{1 - q} = \frac{N_\alpha}{N_\beta}. \quad (72.3)$$

For given values of N_α and N_β , the molecules are assumed to be distributed at random among the available sites, so that the state of disorder is homogeneous throughout the system. Hence, if the number of β -sites surrounding any α -site in the lattice is z , the number of occupied β -sites adjacent to any one molecule on an α -site is $z(1 - q)$; similarly, the number of occupied α -sites around any occupied β -site will be zq .

Suppose the energy of interaction of each pair of molecules on adjacent α - and β -sites is w ; it will be a function of the distance between the two sites, and consequently on the volume of the system as a whole. This fact brings the treatment of fusion into the classification of cooperative phenomena (cf. Section 70a). It is probable that w will decrease as the degree of disorder increases, but for simplicity the approximation will be made of taking w as

remaining constant. The average energy w_α of a molecule on an α -site as a result of its $z(1 - q)$ immediate neighbors on β -sites will thus be given by

$$w_\alpha = wz(1 - q), \quad (72.4)$$

while the average energy w_β of a molecule on a β -site will be

$$w_\beta = wzq. \quad (72.5)$$

The average energy Δw required to remove an atom from an α -site and to transfer it to a β -site is thus

$$\Delta w = w_\beta - w_\alpha = wz(2q - 1). \quad (72.6)$$

In a state of complete order, when $q = 1$, this becomes equal to wz , as it should; on the other hand, in the state of complete (long range) disorder, when $q = \frac{1}{2}$, this energy is zero, since there is an equal probability of α - and β -sites becoming occupied. In general, the total energy W of interaction due to disorder is given either by $N_\alpha w_\alpha$ or by $N_\beta w_\beta$, which must be identical; hence, from equations (72.1) and (72.4), or from equations (72.2) and (72.5),

$$\begin{aligned} W &= N_\alpha w_\alpha = N_\beta w_\beta \\ &= Nwzq(1 - q). \end{aligned} \quad (72.7)$$

The number of ways of distributing the molecules among the sites so that there are N_α on the α -sites and N_β on the β -sites is given by

$$\begin{aligned} g(q) &= \frac{N!}{(N - N_\alpha)!N_\alpha!} \cdot \frac{N!}{(N - N_\beta)!N_\beta!} \\ &= \left[\frac{N!}{(Nq)!\{N(1 - q)\}!} \right]^2. \end{aligned} \quad (72.8)$$

Since the energy of interaction in the corresponding state of disorder is given by equation (72.7), it follows that the factor Q'' which must be introduced into the partition function to allow for disorder, that is, the appropriate contribution to the configuration integral, is then

$$Q'' = g(q)e^{-W/kT}, \quad (72.9)$$

where $g(q)$ is defined by equation (72.8) and W by equation (72.7). If Q' represents the partition function of the system of N molecules when each is confined to an α -site, so that the system is in a state of perfect order, the complete partition function of the system will then be

$$\begin{aligned} Q &= Q''Q' \\ &= g(q)e^{-W/kT}Q'. \end{aligned} \quad (72.10)$$

Utilizing the values of $g(q)$ and of W derived above, it is found that the partition function defined by equation (72.10) has a maximum for a definite

value of q given by

$$\frac{zW(2q - 1)}{2kT} = \ln \frac{q}{1 - q}, \quad (72.11)$$

or

$$2q - 1 = \tanh zW \frac{2q - 1}{4kT}. \quad (72.12)$$

If $zW/4kT$ is less than or equal to unity, this equation has only one root, namely $q = \frac{1}{2}$, and this corresponds to complete disorder; when $zW/4kT$ is greater than unity, however, there is an additional root, and this determines the maximum value of the partition function for the given degree of disorder. When W/kT is very large, q approaches unity and the system is in a state of almost perfect order.

When the partition function is a maximum, the corresponding free energy will be a minimum, as is apparent from equation (67.8); this evidently represents the equilibrium, or most probable, state of the system. Hence, equations (72.11) or (72.12) may be taken as giving the condition for the actual (most probable) state of the solid-liquid system for a particular value of the interaction energy W .

72d. Free Energy and Pressure.—For a liquid, the free energy F and the maximum work function A are almost identical, since PV_i is small; hence, it is possible to write

$$\begin{aligned} F \approx A &= -kT \ln Q \\ &= -kT \ln \{g(q)e^{-W/kT}Q'\} \\ &= -kT \ln g(q) + W - kT \ln Q', \end{aligned} \quad (72.13)$$

where q , used in defining $g(q)$ and W , is given by equation (72.11). Applying the Stirling approximation to equation (72.8), it is found that

$$\ln g(q) = -N\{2q \ln q + 2(1 - q) \ln (1 - q)\} \quad (72.14)$$

and hence,

$$F \approx A = NkT\{2q \ln q + 2(1 - q) \ln (1 - q)\} + Nwzq(1 - q) - kT \ln Q'. \quad (72.15)$$

In the completely ordered state $q = 1$, and then the first two terms on the right-hand side are zero, and the free energy is equal to the last term only; the first two terms, therefore, represent the contribution due to disorder.

It is convenient, although not necessarily correct, to divide the free energy into two independent terms; one indicated by F' (or A'), which is appropriate for an ordered system of molecules, and the other by F'' (or A'') representing an additional contribution resulting from disorder in the distribution of the molecules among the α - and β -sites; thus,

$$F = F' + F''$$

and

$$A = A' + A'',$$

where

$$F' \approx A' = -kT \ln Q' \quad (72.16)$$

and

$$F'' \approx A'' = NkT\{2q \ln q + 2(1-q) \ln (1-q)\} + Nwzq(1-q). \quad (72.17)$$

The value of q is a function of w/kT only, as is shown by equations (72.7) and (72.11); hence, if w were known, it should be possible to evaluate F'' (or A''). This matter will be taken up shortly, but in the meantime it is necessary to consider the partition function Q' . In the derivation of the configuration integral of a system of N molecules confined to cells of average volume V/N , in Section 70b, it was assumed that the molecules could move freely from one cell to another. However, for a completely ordered state, it is necessary to suppose that each molecule is restricted to its own cell; in this case the configuration integral Q_u is given by

$$Q_u = Q_u^N,$$

in which Q_u is defined by equation (70.25), and consequently

$$\begin{aligned} \ln Q_u &= N \ln Q_u \\ &= N \ln 2\pi\gamma g \frac{V}{N} + \frac{N\epsilon_0}{kT}, \end{aligned} \quad (72.18)$$

where ϵ_0 is given by equation (70.28). The value of $\ln Q_u$ here differs from that in equation (70.27), and hence from equation (70.29), by the term N ; in other words, the integer 1 in the latter equation should be omitted for a perfectly ordered state. The complete partition function Q' for a system of N molecules in a state of perfect order is thus

$$Q' = \left\{ \frac{(2\pi mkT)^{3/2}}{h^3} \right\}^N Q_u Q_i, \quad (72.19)$$

where Q_u is defined by equation (72.18), and Q_i , equal to Q_i^N , refers to the contribution of the internal degrees of freedom. It follows, therefore, that

$$\begin{aligned} F' \approx A' &= -kT \ln Q' \\ &= -NkT \ln \frac{(2\pi mkT)^{3/2}}{h^3} - NkT \ln 2\pi\gamma g \frac{V}{N} \\ &\quad - \frac{N\epsilon_0}{kT} - NkT \ln Q_i, \end{aligned} \quad (72.20)$$

which differs from equation (70.38) by the term $-NkT$.

The pressure also may, conveniently, be expressed as the sum of two terms, and this can be done by utilizing the thermodynamic equation

$$P = - \left(\frac{\partial A}{\partial V} \right)_T.$$

If P' is the pressure of an ordered system, and P'' is the additional effect arising from disorder, then

$$P' = - \left(\frac{\partial A'}{\partial V} \right)_T = kT \left(\frac{\partial \ln Q'}{\partial V} \right)_T.$$

Since all the factors in Q' , other than Q_u , are independent of the volume,

$$P' = kT \left(\frac{\partial \ln Q_u}{\partial V} \right)_T, \quad (72.21)$$

and this has exactly the same value as given by equation (70.31); it was noted, in fact, in Section 70c that the expression derived there for the pressure is independent of any assumption as to the availability of the space to the N molecules. Nevertheless, according to the arguments developed here, this is not the only contribution to the pressure, for there must be added P'' determined by

$$\begin{aligned} P'' &= - \left(\frac{\partial A''}{\partial V} \right)_T \\ &= - \left(\frac{\partial A''}{\partial q} \right)_{V,T} \left(\frac{\partial q}{\partial V} \right)_T - Nzq(1-q) \frac{dw}{dV}, \end{aligned}$$

since w for the postulated model is a function of the volume alone. Since the system under consideration is in equilibrium, at least as far as order-disorder is concerned, the work function A'' will be a minimum at constant volume and temperature; that is to say,

$$\left(\frac{\partial A''}{\partial q} \right)_{V,T} = 0,$$

and hence equation (72.21) reduces to

$$P'' = - Nzq(1-q) \frac{dw}{dV}. \quad (72.22)$$

72e. Theory of the Melting Point.—The discussion in the foregoing sections is sufficient to permit an understanding of how the order-disorder model leads to the solid-liquid transformation at the melting point. If a quantity n'' is defined by

$$n'' = Nzq(1-q), \quad (72.23)$$

then according to equation (72.22),

$$P'' = - n'' \frac{dw}{dV}. \quad (72.24)$$

(The physical significance of n'' can be readily shown to be the number of

pairs of molecules occupying adjacent α - and β -sites.) As already seen, q is a function of w/kT only, and w is a function of volume only; hence, for a given temperature n'' is a function of the volume alone. For small volumes, w is presumably large, because of repulsive forces between the molecules; according to equation (72.12), q then approaches unity, and by equation (72.23) it follows that n'' will be small. As the volume is increased, w decreases and at the same time n'' increases to a limit of $zN/4$ for $q = \frac{1}{2}$. At this point, long-range order has disappeared completely, although short-range order may still exist. It is seen, therefore, that with increasing volume, n'' increases to a maximum (constant) value as the disorder increases.

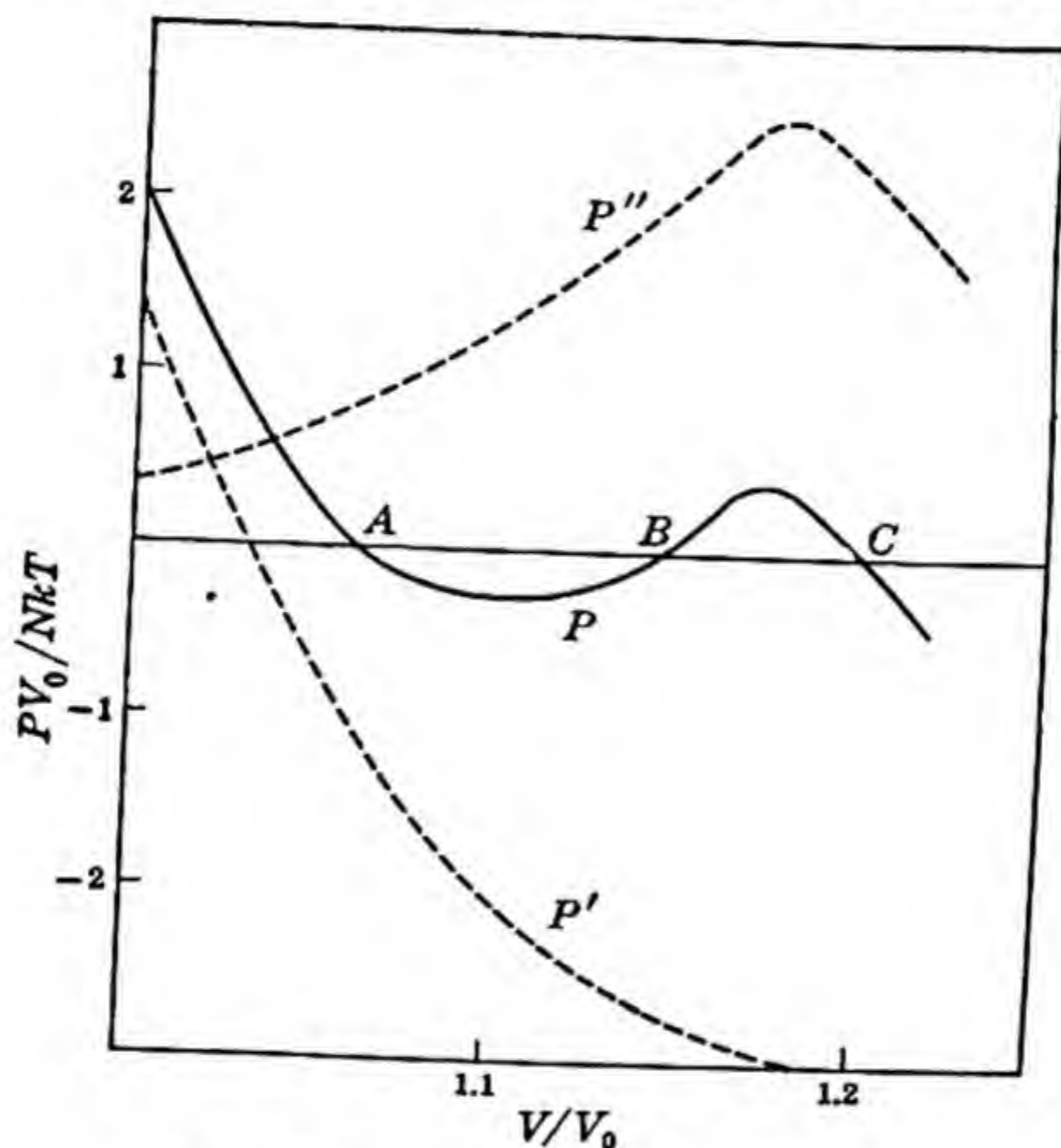


FIG. 59. Theory of the melting point

The other factor, dw/dV , in equation (72.24), however, would be expected to decrease steadily as the volume increases, provided the forces contributing to w are repulsive. It follows, therefore, that P'' should increase to a maximum and then decrease again as the volume of the system is increased. On the other hand, P' , as determined by equation (70.21), decreases steadily as the volume becomes larger, at constant temperature, as shown in Fig. 59. The total pressure is obtained by summing the values of P' and P'' for each volume. It is at once evident that the curve is sigmoid in shape, like the isotherms which represent the change in phase from gas to liquid (cf. Fig. 51). At a certain pressure, therefore, there are two points, A and C , corresponding to states of equal free energy, i.e., where $\int VdP$ is the same, and which consequently represent two systems in equilibrium at the same temperature.

As in the case of condensation, the system will actually follow the direct path AC , rather than the sigmoid path, as the volume changes, since the latter would involve an increase of free energy in passing from A to B , followed by an equal decrease from B to C . It is apparent, therefore, that the points A and C must correspond to two phases in equilibrium at a definite temperature and pressure. The two points presumably represent solid (A) and liquid (C), respectively, and the temperature would give the melting point at the given pressure. At a different temperature there would be a different isotherm; hence, the points A and C at which the free energies are equal would occur at a different pressure, indicating a change of melting point with pressure.

It is evident, therefore, that the concept of varying order-disorder as the volume of a solid-liquid system changes at constant temperature is able to account for the phenomenon of melting. At the point A , which represents the solid just before it melts, the system is in a state of comparative, although not complete, order, while at C , which corresponds to the liquid just after melting, there is considerable disorder. Points along the line AC represent a mixture of solid and liquid phases in equilibrium, and the transition from A to C corresponds to a state of disorder gradually sweeping through the system as the volume increases at constant temperature and pressure. The existence of two points with the same free energy, that is, the sigmoid shape of the isotherm, is to be attributed to the shape of the P'' curve in Fig. 59, and this is due to a combination of circumstances. These are first, the increase of n'' to a maximum, which implies increasing disorder, with increasing volume at constant temperature and external pressure; and second, the steady decrease in dw/dV at the same time, this being a manifestation of the cooperative phenomenon referred to in the introductory Section 72a.

72f. Calculation of Properties at Melting Point.—Since the proposed model is able to give a qualitative interpretation of melting, it is of interest to see how far it can reproduce quantitatively the experimental results associated with melting. In order to do this it is necessary to know the interaction energy w as a function of the volume; it is then possible to derive both q and dw/dV , which are required for the evaluation of the complete partition function. The reasonable assumption is made at the outset that the interaction energy w between molecules on adjacent α - and β -sites is determined entirely by the repulsive part of the intermolecular forces; if the repulsive field is assumed to fall off in proportion to the inverse twelfth power of the intermolecular distance, as in previous discussions (cf. Section 70), it is possible to write

$$w = w_0 \left(\frac{r_0}{r} \right)^{12} \quad (72.25)$$

$$= w_0 \left(\frac{V_0}{V} \right)^4, \quad (72.26)$$

where r_0 refers to the intermolecular distance in the equilibrium state of the

system, i.e., in the state of minimum potential energy, and V_0 is the corresponding molar volume, i.e., $V_0 = \frac{4}{3}N\pi r_0^3$. No method is yet available for the theoretical calculation of w_0 , although this might be achieved by wave mechanics, and so it is estimated by means of one observable quantity, viz., either the temperature of melting, the change of volume on melting, or the latent heat (or entropy) of fusion.

If the pressure P is taken as the sum of P' and P'' , then by equations (72.21) and (72.22)

$$\frac{PV}{NkT} = \frac{V}{N} \left(\frac{\partial \ln Q_u}{\partial V} \right)_T - \frac{zV}{kT} q(1-q) \frac{dw}{dV}. \quad (72.27)$$

On differentiation of equation (72.26) with respect to V , it is seen that

$$\frac{dw}{dV} = - \frac{4w_0 V_0^4}{V^5},$$

and combination of this with equation (72.27) gives the equation of state

$$\frac{PV}{NkT} = \frac{V}{N} \left(\frac{\partial \ln Q_u}{\partial V} \right)_T + \frac{4zw_0}{kT} q(1-q) \left(\frac{V_0}{V} \right)^4. \quad (72.28)$$

The foregoing derivations are undoubtedly more strictly applicable to non-polar molecules, for the intermolecular force fields would then have no marked directional effects. Under these conditions α - and β -sites would have equal probability, as has been postulated, at temperatures above the melting point. For nonpolar molecules, particularly if they have spherical symmetry, the packing in the liquid would be of the face-centered type, as was assumed in Section 70; the value of z in equation (72.28) would then be 6, and γ required for the evaluation of Q_u would be $\sqrt{2}$.

The method employed to determine w_0 is to find by a process of trial and error the value which will give the correct condition for the melting point at any given pressure. The procedure would presumably be somewhat as follows: a value of w_0 is chosen arbitrarily, and then with the aid of equation (72.28) the isotherm PV_0/NkT is plotted as a function of V/V_0 , as in Fig. 59, for the known melting point of the substance at a definite pressure, e.g., zero pressure. This particular pressure must then give the points A and C with the same free energy; that is to say, the area enclosed by the actual isotherm and the straight line AB must be equal to that enclosed by the isotherm and the line BC , if the value of w_0 has been chosen correctly. It is of interest to record that w_0 is approximately equal to u_0 , the potential energy at the minimum of the potential energy curve for a pair of molecules (cf. Section 69a); this is not altogether surprising, since w_0 is supposed to represent the interaction energy between two molecules occupying adjacent α - and β -sites, whereas u_0 is the average energy of interaction between any pair of molecules in a gas (or liquid) at the same distance (r_0) apart.

Once w_0 is known, it is possible to calculate various properties associated with melting by means of the equations already developed; for example, the melting pressure at any temperature can be obtained from equation (72.28). From the isotherm of PV_0/NkT against V/V_0 , the volume of the liquid at zero pressure can be calculated for the given temperature; further, since the volume at the known melting point for zero pressure can also be obtained, it is possible to evaluate the coefficient of expansion of the liquid.

The entropy of the system at any pressure may be determined in various ways, the most obvious being by means of the thermodynamic equation

$$S = - \left(\frac{\partial A}{\partial T} \right)_v,$$

the value of A , equal to $A' + A''$, being given by equations (72.17) and (72.20). It may be noted that the corresponding entropies S' and S'' , the former representing the contribution of the ordered system while the latter is due to disorder, may be derived separately from A' and A'' , respectively. The entropy of fusion is the difference in the values at the two points A and C (Fig. 59) which represent solid and liquid, respectively, at the melting temperature and pressure. Incidentally, from the values of the abscissae (V/V_0) at these two points, the molar volumes of solid and liquid can be obtained; V_0 is taken as $\frac{1}{3}N\pi r_0^3$, where r_0 is derived from the second virial coefficient of the gas. The results calculated for argon are compared with the experimental data in Table XXIX; the general agreement indicates that there is some basis for the view that melting can be accounted for in terms of molecular forces in the manner described above.

TABLE XXIX. MELTING PROPERTIES OF ARGON

	Calc.	Obs.
Molar Volume of Liquid	29.6	28.0 cc.
Molar Volume of Solid	26.3	25.1 cc.
Coefficient of Expansion	0.004	0.0045
Melting Pressure at 90.3° K	286×10^6	291×10^6 dynes/cm. ²
Entropy of Melting	$1.70 R^*$	$1.66 R$

* $S' = 0.8R$, $S'' = 0.9R$.

72g. Partition Function of Liquid Above Melting Point.—At temperatures above the melting point, the fraction q attains its limiting value of $\frac{1}{2}$; under these conditions the limiting value of Q'' , which is the contribution to the partition function due to disorder, given by equation (72.9) as

$$\begin{aligned} \ln Q'' &= \ln g(q) - \frac{W}{kT} \\ &= -N\{2q \ln q + 2(1 - q) \ln (1 - q)\} - \frac{W}{kT}, \end{aligned}$$

becomes, with $q = \frac{1}{2}$,

$$\ln Q'' = N(2 \ln 2) - \frac{W}{kT}. \quad (72.29)$$

By equation (72.7), W is equal to $Nwzq(1 - q)$, and since q is $\frac{1}{2}$, it follows that

$$W = \frac{1}{4}Nwz,$$

and hence,

$$\ln Q'' = N \left(2 \ln 2 - \frac{wz}{4kT} \right) \quad (72.30)$$

$$= N \left\{ 2 \ln 2 - \frac{w_0 z}{4kT} \left(\frac{V_0}{V} \right)^4 \right\}. \quad (72.31)$$

This contribution to the logarithm of the partition function due to disorder, based on the order-disorder model, may be compared with the constant contribution N required by the cell model (cf. Section 70b), assuming the whole volume of the liquid to be available to each molecule. If $wz/4kT$ is zero, then $\ln Q''$ will be $1.38N$; on the other hand, $wz/4kT$ cannot exceed unity, for $q = \frac{1}{2}$, and so the smallest value of $\ln Q''$ will be $0.38N$. As a general rule, $wz/4kT$ will be less than unity, and the value of $\ln Q''$ will approach the higher rather than the lower limit. Although the difference between the actual value of $\ln Q''$, as given by equation (72.30) or (72.31), and that, namely N , used in the previous treatment may, therefore, not be great, it is evident that the calculations of vapor pressures and boiling points in Section 70d cannot be exactly the same as those based on the new model. The molar free energy of the liquid F_l is given by

$$F_l = F' + F'',$$

where F' and F'' are defined by equations (72.20) and (72.17), respectively, while for the vapor F_g is given, as usual, by equation (70.39); if the values of F_l and F_g are equated, the pressure involved in the latter is the equilibrium vapor pressure of the liquid. The result is

$$\begin{aligned} \ln p = & - \ln \frac{2\pi\gamma g}{NkT} V_l - \epsilon_0 \\ & - NkT \{ 2q \ln q + 2(1 - q) \ln (1 - q) \} + Nwzq(1 - q). \end{aligned} \quad (72.32)$$

In order to evaluate the boiling point, p is equated to 1 atm., and the corresponding temperature is calculated; the entropy of vaporization may also be derived in the manner already described. To make use of equation (72.32), the first two terms on the right-hand side are calculated by the procedure given in Section 70d; the last two terms depend on w , since q is a function of

TABLE XXX.¹⁹ CALCULATED BOILING POINTS AND ENTROPIES OF VAPORIZATION

Liquid	Boiling Point		Entropy of Vaporization	
	Calc.	Obs.	Calc.	Obs.
Argon	87.3° K	87.4° K	17.5 cal.	17.2 cal.
Nitrogen	75.0°	77.2°	16.7	17.3

¹⁹ The data in this table were derived from a somewhat different treatment of order-disorder, but the results for the present treatment are probably almost the same.

w only. The latter is determined from equation (72.26), with w_0 derived from one of the melting point properties as in Section 72f. The boiling points and entropies of vaporization of argon and nitrogen calculated in this way are recorded in Table XXX; these may be compared with the results in Table XXVII based on the cell model, with the whole volume of the liquid assumed to be available to all the molecules.

73a. Liquid as Intermediate Between Solid and Gas: Holes in Liquids.²⁰

—An alternative attempt to allow for the gradual, rather than the sudden, change from complete order to complete disorder as the temperature of the system is raised is based on the treatment of a liquid as intermediate between a gas and a solid. A partition function for a liquid is constructed in such a manner that it goes over into that of a gas at one extreme, and into that of a solid at the other extreme. The fundamental bases of the arguments are derived from a consideration of the viscosities of liquids. There is evidence to indicate that the viscosity of a normal liquid under ordinary conditions is merely a function of the volume. Viscosity is believed to depend on the number of "holes" available to the molecules in the liquid state, and hence it has been argued that the number of holes increases approximately in proportion to the volume, as the temperature is raised. These holes are somewhat analogous to the β -sites referred to in Section 72a, etc., but there is an important difference between the view now being considered and that previously described. According to the earlier discussion, the number of new equilibrium positions (β -sites) that become available on melting is equal to the number of molecules in the system, but in the present treatment it is postulated that the number of holes in the liquid is a linear function of the volume and may be increased almost without limit.

If v_h is the volume of a hole, then the number n_h of holes per mole of liquid is given by

$$n_h = \frac{V - V_s}{v_h} \quad (73.1)$$

where V and V_s are the molar volumes of liquid and solid, respectively. The process of liquefaction is thus regarded as the introduction of holes into the solid, which is supposed to contain no holes available for molecules to move into. The effective volume of a single molecule will be equal to V_s/N , where N is the total number of molecules in the system, and if the volume of a hole is $1/n$ th of the volume of a molecule, it follows that

$$v_h = \frac{V_s}{nN}, \quad (73.2)$$

and combination with equation (73.1) gives

$$\frac{n_h}{N} = n \frac{V - V_s}{V_s}. \quad (73.3)$$

²⁰ Roseveare, Powell and Eyring, *J. App. Phys.*, **12**, 669 (1941).

The fraction n_h/N is the ratio of the number of holes to the number of molecules, and this may be represented by the symbol γ , so that

$$\gamma = n \frac{V - V_s}{V_s}. \quad (73.4)$$

A liquid is regarded as a mixture of N molecules, equivalent to α -sites, and n_h holes, equivalent to β -sites; the entropy of random mixing of the molecules and holes would then be equal to the entropy of fusion, so that

$$\begin{aligned} \Delta S_f &= -Nk \ln \frac{N}{N + n_h} - n_h k \ln \frac{n_h}{N + n_h} \\ &= Nk \left\{ \ln(1 + \gamma) + \gamma \ln \frac{1 + \gamma}{\gamma} \right\}. \end{aligned} \quad (73.5)$$

Therefore, if the ΔS_f per mole is known, γ can be calculated, with N taken as the Avogadro number. It has been seen (Section 70f) that the entropy of fusion of metals and of some other substances, whose molecules rotate in both the liquid and solid states, is about 2 cal. per degree per mole; for such substances γ is calculated to be 0.54, so that at the melting point the number of holes introduced is about half the number of molecules present. It should be noted that if γ is known, it is possible to calculate n by means of equation (73.4); for this purpose the molar volumes of solid and liquid at the melting point are required. For most normal liquids n is about 6, but for liquid metals it is three or four times as large.

73b. Partition Function for Liquid.²¹—The partition function of the liquid phase is regarded as made up of a combination of the partition functions of the molecules and of the holes in a suitable proportion. The molecules may be treated as occupying equilibrium positions (α -sites) that are equivalent to those in the solid state; assuming the molecules in the solid to act as simple (localized) three-dimensional harmonic oscillators, the partition function Q_s per molecule may then be given by [cf. equation (67.12)] an expression of the Einstein type, viz.,

$$Q_s = (1 - e^{-h\nu/kT})^{-3} e^{-3h\nu/2kT} e^{E_s/RT}, \quad (73.6)$$

where the vibration frequency ν is related to the Einstein characteristic temperature θ_E in the usual manner, i.e., $h\nu/k = \theta_E$. The term $e^{-3h\nu/2kT}$ is that for the zero-point energy, while E_s represents the average potential energy (per mole) of the molecules in their equilibrium positions in the solid state. The holes (β -sites) are regarded as analogous to the molecules in a gas, each hole being treated as a molecule occupying the volume V_s/Nn ; hence, the partition function Q_o in one of the gas-like equilibrium positions will be represented by

$$Q_o = \frac{(2\pi mkT)^{3/2}}{h^3} \cdot \frac{V_s}{Nn} e^{-E_s/RT}, \quad (73.7)$$

²¹ Eyring and Walter, *J. Chem. Phys.*, 9, 393 (1941).

where δE_s is the energy required to form a hole. The factor δ is a function of the volume which will be considered shortly.

The most stable configuration of molecules and holes is assumed to be the one in which the molecules are distributed among the two kinds of equilibrium positions in a ratio equal to their volume fractions; thus, the number of molecules in the solid-like positions is proportional to V_s/V , while the number in the gas-like positions is proportional to $(V - V_s)/V$. With this assumption, and introducing the a priori probability factor $(N + n_h)!/N!n_h!$ to allow for the number of ways in which N molecules can be distributed among $N + n_h$ equilibrium positions, that is, to allow for order-disorder, the resulting partition function for a system of N molecules becomes

$$Q = \{Q_s^{V_s/V} Q_g^{(V-V_s)/V}\}^N \frac{(N + n_h)!}{N!n_h!}. \quad (73.8)$$

In the solid state, n_h is zero, and V is then equal to V_s ; the partition function in these circumstances reduces to Q_s^N , as it should do. At the other extreme, in the gaseous state, n_h is very large in comparison with N , and V_s is negligible in comparison with V ; under these conditions, equation (73.8) becomes

$$Q = \frac{1}{N!} Q_g^N, \quad (73.9)$$

which is the correct form for a system of N molecules constituting an ideal gas. It is evident, therefore, that as far as considerations of order and disorder under extreme conditions are concerned, the partition function given by equation (73.8) is satisfactory. Making use of the equation for the maximum work function,

$$A = -kT \ln Q,$$

and introducing the Stirling approximation for the factorials, it is found that

$$A = -RT \left\{ \frac{n}{n+\gamma} \ln Q_s + \frac{\gamma}{n+\gamma} \ln Q_g + \ln(1+\gamma) + \gamma \ln \frac{1+\gamma}{\gamma} \right\}. \quad (73.10)$$

To employ equation (73.10) to calculate other properties of a liquid, it is necessary to derive an expression for the factor δ in equation (73.7). If the equations for the partition function and the work function are to go over smoothly into those for an ideal gas, δ must vanish for large volumes, so that $e^{-\delta E_s/RT}$ becomes equal to unity. From viscosity studies, it appears that the energy required to make a hole in a liquid is greater than would be expected from its volume; thus the size of a hole is about one-sixth of a molecule, but the energy required to form the hole is about one-third of that necessary to introduce a hole of molecular size. From these and other empirical considerations, the function

$$\delta = \left(\frac{V_s}{V} \right)^2 \left(2\gamma + \frac{1}{n-1} \right)^{-1} \quad (73.11)$$

has been proposed. For normal liquids, at temperatures appreciably above the melting point, 2γ is much greater than $1/(n-1)$, and under these conditions it is found that

$$\delta E_s = E_s \left\{ \frac{V_s}{V} - \frac{1}{2n} \left(\frac{V_s}{V} \right)^2 \right\}. \quad (73.12)$$

The value of E_s can be calculated from the vapor pressure of the solid at the melting point, making use of the expression for this pressure in terms of the partition function. Since n can be derived from the entropy of fusion, and γ at any molecular volume can be calculated from n by means of equation (73.4), all the information is available for evaluating the partition function, and hence the thermodynamic properties, of the liquid.

The melting point can be determined by finding the temperature at which the vapor pressures of solid and liquid are equal, and the entropy of melting can be estimated in the usual manner as the difference between the entropies of solid and liquid states at the melting point. By plotting the maximum work function \mathcal{A} against the volume and determining the two points at which the curve has a common tangent, the volume of the two phases (liquid and vapor) in equilibrium, as well as the corresponding vapor pressure, could have been determined. However, the calculations were simplified in practice by approaching the problem from a less fundamental standpoint, making use of the van der Waals equation.

73c. Equation of State.—An equation of state can be obtained by differentiating the maximum work function, as given by equation (73.10), with respect to the volume at constant temperature; introducing equation (73.12), the result is

$$\begin{aligned} P &= - \left(\frac{\partial \mathcal{A}}{\partial V} \right)_T \\ &= \frac{RT}{V_s} \left[n \ln \frac{1+\gamma}{\gamma} + \left(\frac{V_s}{V} \right)^2 \ln \frac{Q_0}{Q_s} \right. \\ &\quad \left. - \frac{E_s}{RT} \left\{ \left(\frac{V_s}{V} \right)^2 - \frac{3}{2n} \left(\frac{V_s}{V} \right)^4 \right\} \right]. \quad (73.13) \end{aligned}$$

This is a van der Waals type of equation, and the critical temperature, pressure and volume can be determined by finding the conditions for which the P - V isotherm has a point of inflection.

The general methods just described were applied to argon and nitrogen, and the volumes (V_l) and vapor pressures of the liquids at a series of temperatures, the critical constants, and the temperature (T_f), volume change (ΔV_f) and entropy of fusion (ΔS_f) were calculated. Some of the results are compared with the experimental data in Table XXXI. Similar calculations were made for benzene, after applying a correction for restricted rotation in the solid state which passes over into free rotation in the liquid; as in

Table XXXI, the results agreed well with those observed experimentally. Attention should be called, however, to the fact that the computations are based on the value of γ , and also require a knowledge of the vapor pressure

TABLE XXXI. CALCULATED PROPERTIES OF LIQUIDS

Argon					
Melting Phenomena			Critical Phenomena		
	Calc.	Obs.		Calc.	Obs.
T_f	82.9°	83.85° K	T_c	154.2°	150.7° K
V_f	28.27	28.03 cc.	V_c	78.7	75.3 cc.
ΔV_f	3.14	3.05 cc.	P_c	59.4	48.0 atm.
ΔS_f	3.40	3.35			

Nitrogen					
Melting Phenomena			Critical Phenomena		
	Calc.	Obs.		Calc.	Obs.
T_f	62.86°	63.14° K	T_c	141.0°	126.0° K
V_f	31.84	31.95 cc.	V_c	90.3	90.1 cc.
ΔV_f	2.49	2.64 cc.	P_c	48.4	33.5 atm.
ΔS_f	2.64	2.73			

at the melting point to derive E_s , and of the characteristic temperature to obtain ν ; in addition the value of the factor δ is given by an expression that is largely empirical in character. Nevertheless, the treatment of the liquid state as intermediate between a gas and a solid appears to present some interesting possibilities.

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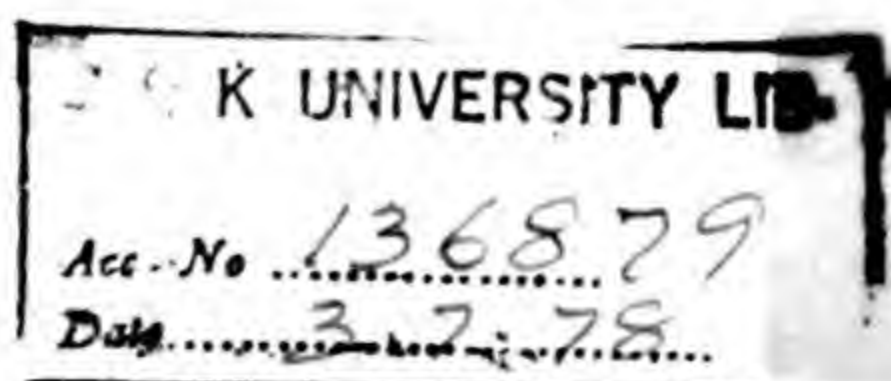
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